

SYNTHESIS AND PROPERTIES OF HALOGEN CONTAINING
SIMPLE AND COMPLEX BLOCK COPOLYETHERSArsen Kharaev^{1, *}, Raisa Oshroeva¹, Gennady Zaikov², Rima Bazheva¹,
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Abstract. Bifunctional halogen-containing oligomers of various composition and structure were synthesized. Simple and complex aromatic block copolyethers of constructional and film purpose were obtained by various methods of polycondensation. Physical and chemical properties of obtained block copolyethers were studied.

Keywords: bifunctional oligomer, polycondensation, thermal resistance, fire resistance.

1. Introduction

From numerous references it is known, that simple and complex polyethers have a number of unique properties. So, such simple polyethers as polyethersulphones, polyetherketones and others, possess the high thermal resistance and plasticity in combination with some other operational characteristics. At the same time complex polyethers are characterized by high heat resistance and increased rigidity.

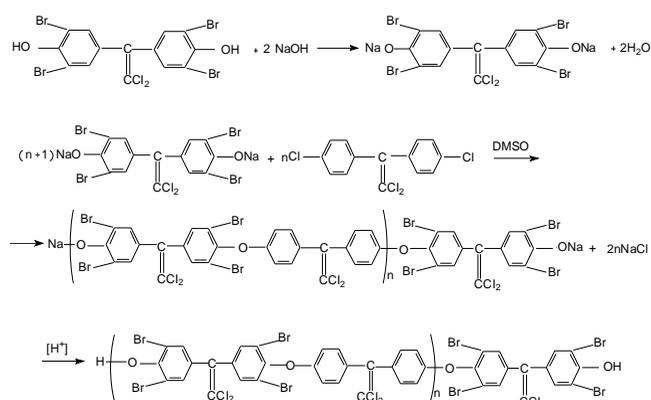
The presence of multiple bonds in a macrochain makes these polymers capable of formation of spatially structured materials distinctive by higher operational properties. By this way it is possible to increase considerably the thermal resistibility of materials that expand an operation temperature range of its products, to raise the thermooxidizing destruction start temperature by tens degrees, to improve strength properties, to obtain polymeric materials, resistant even to the concentrated solutions of acids and alkalia.

Inserting halogen atoms into the structure of macromolecular chain significantly increases the fire resistance of polymers. At their significant amounts the

polymers become nonflammable and they are not secondary sources of ignition, because they do not burn and do not sustain burning. The content of atoms of halogen also positively influences mechanical, thermal, physical and other properties. Presence of voluminous polar atoms of bromine raises strength characteristics of polymers. Polar atoms of bromine also expand a temperature range of products operation due to the increase in glass transition and melting or softening temperature. Showing the shielding effect, atoms of bromine increase polyethers resistance to solutions of various acids and alkalia, including concentrated ones [1].

2. Experimental

For obtaining the unsaturated halogen-containing block copolyethers by high-temperature polycondensation various new oligoethers [2, 3] were synthesized according to the following scheme ($n = 1-20$):

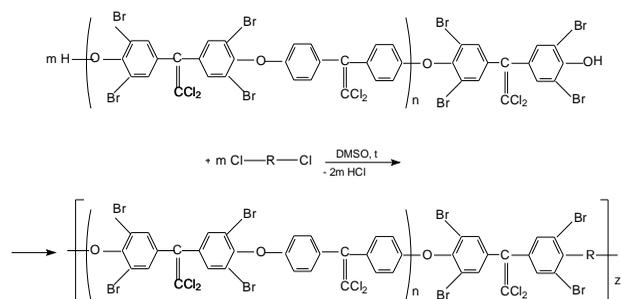


The reaction between 1,1-dichloro-2,2-di (3,5-dibrom- n -hydroxy-phenyl)ethylene and 1,1-dichloro-2,2-di(n -phenyl chloride)ethylene is carried out in the environment of aprotic dipolar solvent – dimethyl sulfoxide (DMSO) in the atmosphere of inert gas (nitrogen).

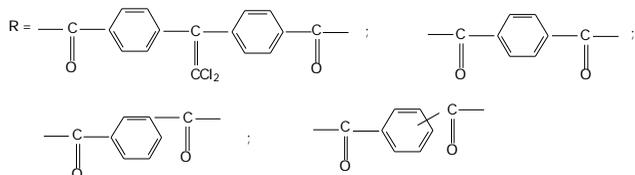
Simple polyethers are obtained by high-temperature polycondensation in N,N -dimethylacetamide at 443–453 K for 6 h in inert gas atmosphere – nitrogen.

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The scheme of polyether obtaining may be presented in a general view as follows:



where:



The viscosity measurements were made according to RF Standards using an Ubbelohde viscometer with $d = 0.56$ mm. The viscosity was measured in 1,2-dichloroethane and the concentration of the solution was 0.5 g/dl.

Mechanical properties of PAEK measured for film specimens (100x10x0.1 mm) were tested (ASTM D638) on a MRS-500 tensile tester with a constant strain rate of 40 mm/min at 293 K. The film specimens were obtained by casting the polymer melt from 1,2-dichloroethane solution to a solid mirror surface followed by evaporation of a solvent.

Thermogravimetric analysis of poly(arylene ether ketone)s was performed on the derivatograph "MOM" under a temperature increase rate at 5 degree/min in the air atmosphere.

The investigation of the polydispersity of the block copolymers was conducted by the turbidimetric titration method on an FEC-56M device. The principle of turbidimetric titration is that the diluted polymeric solution will become turbid if a precipitator is added and will have different optical density from the original solution. The concentration of the solution was 0.01 g/ml;

1,2-dichloroethane was used as a solvent, and isopropyl alcohol – as a precipitator.

Phase transitions (softening temperature) were studied with the use of differential scanning calorimeter DSC 4000 "Perkin Elmer", operated by heat flow comparing with the heating rate of 5 degrees per minute.

The fire resistivity of the polymers was evaluated by the oxygen index method. The oxygen index test carried out on film samples (strips) fixed vertically in the cylindrical chamber through which a laminar stream of nitrogen-oxygen mixture passes. Tests are carried out at various ratios of the gas mixture until the optimum burning of the sample is reached. The sample is set on fire from the top end with the help of a gas torch that is then withdrawn.

3. Results and Discussion

Composition and structure of oligoethers are confirmed by IR-spectroscopy and elemental analysis. Some properties of oligoethers are given in Table 1.

Nonsaturated halogen-containing simple and complex polyethers with block structure were obtained with the use of synthesized oligoetherone [4].

Complex polyethers are obtained by the acceptor catalytic polycondensation using the equimolar quantities of dichloranhydride of tere- and isophthaloyl acids (DHAT/IA) and dichloranhydride of 1,1-dichloro-2,2-di(*n*-carboxy phenyl)ethylene (HAETIK) as acid components. The synthesis was carried out in the ethylene dichloride solution at room temperature with the use of triethylamine as an acceptor catalyst.

Polyethers are obtained quantitatively and with the viscosity in the range of 0.6–0.9 dl/g (Table 2). These indicators together with the data of IR-spectroscopy and turbidimetric titration confirm the formation of polyethers of supposed structure. On IR spectrum there are bands, corresponding to simple ether bonds at 1135 cm^{-1} , isopropilen group in the range of $2960\text{--}2980\text{ cm}^{-1}$, carbonyl group between aromatic rings in the range of $1600\text{--}1675\text{ cm}^{-1}$, $\text{Ar}_2\text{-C=CCl}_2$ at 980 cm^{-1} , C-Br in the range of $500\text{--}600\text{ cm}^{-1}$. Absorption bands, characteristic for OH-groups in the range of $3300\text{--}3600\text{ cm}^{-1}$ are absent.

Table 1

Properties of oligomers

Oligomers	n	Yield, %	$T_{soft.}$, K	Calculated MM	Hydroxyl group content	
					Calculated	Obtained
OE-1TBC-2	1	96	369–370	1446	2.35	2.34
OE-5TBC-2	5	95	375–378	4806	0.71	0.70
OE-10TBC-2	10	95	378–380	9015	0.38	0.37
OE-20TBC-2	20	94	381–383	17433	0.19	0.20

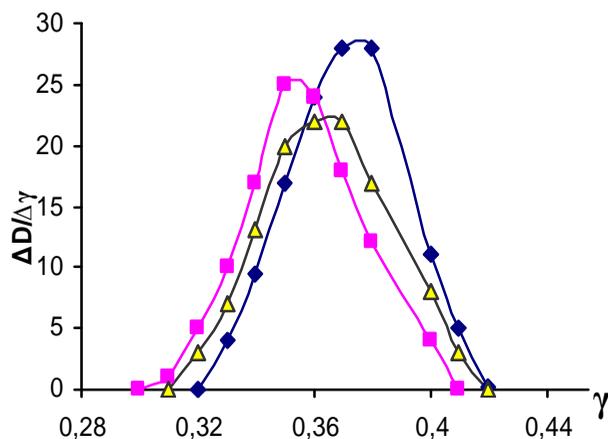


Fig. 1. Differential curves of turbidimetric titration of polyethers: OE-1TBS-2 + HAETIK (■); OE-1TBS-2 + DHAT/IA (▲) and OE-1TBS-2 + DHDPS (◆)

Curves of molecular-mass distributions show a low polydispersity and good solubility of polyethers in chlorinated organic solvents. From Fig. 1 it is visible, that thresholds of polyethers coagulation lie in the field of rather large volumes of solvents that confirm their good solubility. It is shown, that in the ranks of polyethers with the increase of condensation rate of initial oligomers the solubility in organic solvents increases.

Glass transition temperatures of unsaturated bromine containing polyethers on the basis of various dihalogenides are given in Table 2. It is visible, that in the ranks of polyethers this characteristic doesn't change significantly. If some increase of it is observed, it can be explained with prevalence of structuring process in macromolecules because of saturation of a macrochain by a dichloroethylene group, over the process of loosening

structure because of the increase in a share of voluminous atoms of bromine at initial oligomer extending.

The highest values of heat resistance are characteristic for polyethers on the basis of dichloride anhydride of HAETIK. Possibly, it results from insertion the remains of dichloride anhydride $>C=CCl_2$ group in macromolecules. Double link promotes the formation of mesh structure, and atoms of chlorine increase polarity of macromolecules. In the case of other polymers, where in the remains of halogenides there is no dichloride ethylene group, lower indicators of temperatures of glass transition are observed.

Polyethers, obtained in the present work, possess the increased thermal resistance. The thermooxidative destruction of polymers starts in the range of 651–691 K. In the ranks of polyethers with the increase of condensation rate of initial oligomers the increase of thermal stability indicators is observed. In complex polyethers it is related to the reduction of content of thermally unstable complex ether groups. In simple polyethers, which are rather resistant to high temperatures, the decisive factor is the existence of polar and bulk atoms of bromine, and concentration of the latter one increases in ranks.

The manifestation of structuring effect is easily observed when comparing temperatures of 10 % mass loss. In polyethers on the basis of HAETIK it courses a substantial increase of this indicator. Other polymers, which do not contain $>C=CCl_2$ in acid components, loose the specified mass at significantly lower temperatures. Below in Table 3 the results of thermal stability studies and other properties of the synthesized polyethers are presented.

Table 2

Some properties of polyethers

Polymer	Yield, %	Intrinsic viscosity η , dl/g	Glass transition temperature T_g , K
OE-1TBC-2 + HAETIK	98.0	0.81	533
OE-10TBC-2 + HAETIK	98.0	0.80	536
OE-20TBC-2 + HAETIK	96.5	0.63	544
OE-1TBC-2 + DHAT/IA	97.5	0.90	509
OE-10TBC-2 + DHAT/IA	95.0	0.82	512
OE-20TBC-2 + DHAT/IA	95.0	0.66	515
OE-1TBC-2 + DPBP	96.0	0.71	520
OE-10TBC-2 + DPBP	97.5	0.66	524
OE-20TBC-2 + DPBP	96.5	0.60	523
OE-1TBC-2 + DHDPC	97.5	0.75	513
OE-10TBC-2 + DHDPC	96.0	0.70	516
OE-20TBC-2 + DHDPC	96.5	0.61	514

Table 3

Thermal and mechanical properties of polyethers

Polymer			σ_{ts} , MPa	ε , %	OI, %
	2 %	10 %			
OE-1TBC-2 + HAETIK	406	526	96.8	12.6	53.0
OE-10TBC-2 + HAETIK	410	532	99.8	11.1	56.0
OE-20TBC-2 + HAETIK	418	537	101.2	11.0	56.5
OE-1TBC-2 + DHAT/IA	397	471	103.6	11.4	50.5
OE-10TBC-2 + DHAT/IA	402	479	106.7	11.0	52.0
OE-20TBC-2 + DHAT/IA	409	480	106.3	10.2	53.5
OE-1TBC-2 + DPBP	378	480	93.4	11.4	50.0
OE-10TBC-2 + DPBP	394	474	104.3	10.1	50.5
OE-20TBC-2 + DPBP	400	482	105.1	9.6	52.5
OE-1TBC-2 + DHDPC	393	491	97.7	11.8	50.5
OE-10TBC-2 + DHDPC	407	495	101.9	10.7	51.0
OE-20TBC-2 + DHDPC	410	497	102.4	10.8	52.0

All polyethers show high tensile strength at rather small elongation at break. The defining factor is the existence and concentration of bromine atoms. In polyether ranks the concentration of the latter one increases, causing the increase of tensile strength. In the competing processes of a structure loosening and increase of macromolecules polarity, probably, the last prevails.

The same explanation has the low indicators of elongation and decrease of this indicator in ranks with the increase in length of initial oligomers. The tensile strength and elongation at break of synthesized polyethers do not differ significantly and are in the range of 93.4–106.7 MPa and 9.6–12.6 % respectively.

The characteristics of inflammation and combustibility of polymer materials are connected closely with the existence of macromolecules containing halogen atoms in the chain. The introduction of $>C=CCl_2$ groups into the chain and the increase of their percentage in block-copolymers promote the increase of the oxygen index (OI). The ramp OI of block-copolymers with the increase of the content of chlorinated components is apparently connected with the changes of the amount of combustible products, exuded from the unit of block-copolymers volume when burning.

As one would expect, the synthesized polyethers do not burn and do not sustain burning. The fire resistance, estimated in oxygen indexes is in the range of 50.0–56.5 %, and it is the result of the maximum saturation of macrochains by the atoms of halogens, and particularly by bromine atoms. We came to such conclusion because of the increase of OI values in all synthesized ranks of polyethers.

The essential contribution to fire resistance is also made by chlorine atoms contained in HAETIK. For this reason OI indicators for a number of polyethers on the basis of given dihalogenid are higher, than in those, which structures do not have $>C=CCl_2$ group. Polyethers on

open flame just carbonize and are not secondary sources of fire.

4. Conclusions

According to the national economy needs for various polymeric materials with specific properties, effective synthesis methods of oligoethers and polyethers, containing sulphone, ketone and arylate groups were developed. Thus, due to the diversity of chemical structure and properties it is possible to select a material with desired wide range operation characteristics. High performance mechanical properties combined with high thermal, heat and flame resistance allow to recommend these polyethers as engineering and film materials in automotive, aviation and space technologies.

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СИНТЕЗ І ВЛАСТИВОСТІ ГАЛОГЕНВМІСНИХ ПРОСТИХ І СКЛАДНИХ БЛОК-КОПОЛІТЕРІВ

***Анотація.** Синтезовані біфункційні галогенвмісні олігомери різного складу і будови. За допомогою різних методів поліконденсації отримані прості і складні ароматичні блок-кополітери конструкційного та плівкового призначення. Досліджено фізико-хімічні властивості блок-кополітерів.*

***Ключові слова:** біфункційні олігомери, поліконденсація, термостійкість, вогнестійкість.*