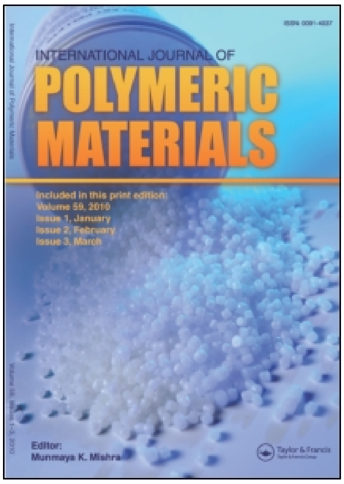

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Polymer-Analogous Conversions of Olefin and Diene Oligomers in Synthesis of Stabilizers for Halogen Containing Polymers

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The polymer-analogous reaction provides an opportunity for the synthesis of new non-toxic and highly effective additives that solve the problems of mono-, diatomic phenols and aminophenols.

KEY WORDS Polymer-analogous conversions, macromolecular stabilizers.

Polymer-analogous reactions are one of the most rapidly developing field of the polymer science. The investigation of chemical conversions involving polymeric products has shown that functionalized macromolecules participate in fine organic synthesis (alkylation, condensation, rearrangement etc.) at higher speed and more selectively than their analogous low molecular agents.[1] This presents new opportunities to modify polymers, create new polymer compositions, synthesize new stabilizers, etc. Of great importance in this case is the increase the spectrum of polymers and the number of reactions that involve new functional groups entering macromolecules.

The use of polymer-analogous reactions for producing high-molecular antioxidants (HAO) based on olefin and diene oligomers is undoubtedly interesting and promising. The synthesis of efficient HMA is very important for the stabilization of the elastomers that possess great molecular mobility and polymers operating at higher temperatures. Under these conditions HMA exhibit the best characteristic of traditional antioxidants (AO) and high-molecular compounds, i.e. uniform distribution in the protected polymer combined with their main merit the nonvolatility. This results in greater protective ability of HAO as compared with the traditional low molecular weight inhibitors.[2]

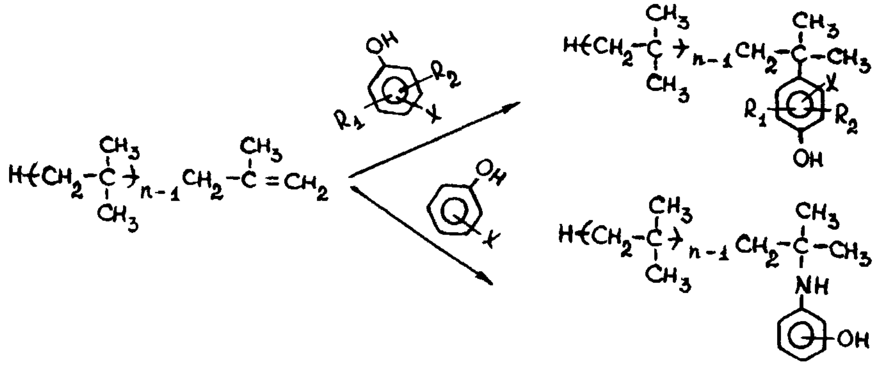
The convenient method of synthesizing phenolic AO is the Friedel-Crafts alkylation[3] of phenols by oligoolefins containing unsaturated $>C{=}C<$ bonds. Many side products are usually formed in the course of this reaction because the alkyl group in the nucleus promotes the subsequent reactions with the electrophylic agent. In particular in the interaction of higher α-olefins with phenol in the presence $ALCL_3$ (35–80°C, 9± hr) the alkylphenol synthesis (up to 80%) is accompanied by the simultaneous formation of the products of their decomposition: aluminum phenoxide and HCL.[4,5]

The process of polymer-analogous reactions of unsaturated teigh-molecular hydrocarbons with phenol is still more complicated due to the secondary processes (isomerization, depolymerization, degradation of initial and functionalized macromolecules), which lead to a large decrease of the final product yield. For instance, in the reaction of poly-α-olefins (M_n = 450 + 2000) with phenol in the presence of benzene sulfonic acid, the yield of poly-α-olefinylphenols did not exceed 46% for PE, 38% polyethylene (PE) polypropylene (PP) and 31% for polyisobutylene (PIB).[6]

The presence of side reactions in phenol alkylations by olefins is characteristic for all catalysts with high relative acidity *B* (B 5.0 mg-eqv K/G), for example, for H_2SO_4, $ZnCl_2$, BF_3, $SnCl_4$, $AlCl_4$ etc.[7] Taking into account the data given in Reference 8 we can assume that the use of compounds with lower B than that of $AlCl_3$ relative acidity as catalysts in particular, of complex salts $Na[AlCl_4]$ (B = 1.6 mg-eqv /g/, $Li[AlCl_4]$ (B = 2.2) and $K[AlCl_4]$ (B = 0.9) may prove to be one of the effective ways of increasing the selectivity of the different phenol alkylation by olefin oligomers and growing up the final product yield.

The synthesis of phenolic HAO has been carried out by alkylation various monohydric and dihydric phenols as well as aminophenols by oligomers of ethylene, propylene, isobutylene, piperylene, copolymers and ternary polymers of ethylene together with propylene.

Principally, any oligomers containing $>C=C<$ bonds in the chain can be used for the HAO synthesis. The scheme of polymer-analogous reactions on the example of oligoisobutylene is as follows:


(1)
(2)

where n = 11 ÷ 63 with the variants:

1. Phenols: a) R_1 = R_2 = X = H; b) R_1 = R_2 = H; X = 2—CH_3; c) R_1 = R_2 = H; X = 3—CH_3; d) R_1 = R_2 =H; X = 4—CH $(CH_3)_2$; e) R_1 = 2—$(CH_3)_3$;

R_2 = 6—$C(CH_3)_3$; X = H. Dihydric phenols: f) $R_1 = R_2$ = H; X = 2—OH; g) $R_1 = R_2$ = H; X = 3—OH; h) $R_1 = R_2$ = H; X = 4—OH. Benzelydenaminophenols: i) $R_1 = R_2$ = H; X = 2—N=CHC_6H_5; j) $R_1 = R_2$ = H; X = 4—N=CHC_6H_5.

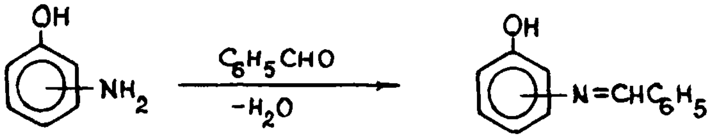
2. Aminophenols: 1) X = 2—NH_2; m) X = 4—NH_2.

Depending on the location and number of the $>C{=}C<$ bonds in the macromolecules of initial oligomers, either the individual compounds with the end phenol group (oligoisubutylene oligomers) or the oligoolephenylphenol blend in accordance with the number and location (inner or end) of the $>C{=}C<$ bonds have been obtained.

The HAO synthesis on the Me[$AlCl_4$] catalysts proceeds in mild conditions. The presence of electron-releasing substitutes (H_2N—, HO—) in the phenol ring facilitates the reactions and increases the yield of final product (Table I).

Introducing bulky substitutes that cause both steric hindrances (—$C(CH_3)_3$) and increase the oligomer molecular mass have resulted in longer reaction time and lower yield of oligoolefinylphenols (Tables I and II). The yield of oligoolefinylphenols was practically independent on the alkaline metal nature in the catalyst (Table I). Therefore, the phenol alkylation was conducted mainly with the help of Na[$AlCl_4$].

Unlike phenols, polymer-analogous reactions of poly-α-olefins with aminophenols in the presence of Me[$AlCl_4$] do not proceed on the aromatic ring but on the aminogroup (Scheme II). Therefore aminophenol was pretreated with benzaldehyde before the hydrocarbon fragment was introduced into the ring:



(3)

The interaction of benzylidene aminophenols with oligoolefins occurred under more severe conditions than that of phenols (Table I). This is linked to the complicated character of the electrophylic substitution caused by the depletion of electrone density of the aromatic ring by the benzylideneaminogroup.

The structure of the synthesized high-molecular phenols has been examined by ^{13}CNMR and IR-spectra. (Table I). In the ^{13}CNMR spectrum of 4-benzylideneaminooligoethylenephenol there is a singlet at 131.5 m.d, characteristic of the carbon atom linked to the N=CHC_6H_5 group and in the spectrum of 4-oligoethylenylaminophenol there is a singlet at 135.3 m.d, characteristic of the carbon atom of the alkyl group, connected with the NH-group. In the IR-spectra of oligoethylenylaminophenols one can observe an absorption band in the range of 3500 cm^{-3} indicating the presence of the secondary aromatic amine.[10] Benzylidenaminoethylenylphenols do not possess the absorption band in the given region.

TABLE I

Polymer-analogous conversions of polyolefines in the presence of Me[AlCl$_4$] (0.05 mol/mol polyolefine, 110°C)

Phenol	Reaction time, hr	Product yield, %	HO-group content, mol/mol polyolefinylphenol	>C=C< bond content, mol/mol polyolefinylphenol	^{13}C NMR-spectra, δ, m.d. (signal of C, linked with the oligomer radical)
1	2	3	4	5	6
Polyethylene					
Catalyst Na[AlCl$_4$]					
Phenol	2,5	96	0,29	0,012	135,5
2-Methylphenol	2,5	95	0,28	0,015	135,2
3-Methylphenol	3,0	93	0,28	0,015	134,8
4-iso-Propylphenol	3,0	93	0,28	0,021	129,6
2,6-di-Tertbutylphenol	4,0	89	0,27	0,033	135,2
1,2-di-Oxybenzene	2,5	93	0,56	0,021	149,0
1,3-di-Oxybenzene	2,5	90	0,54	0,030	131,6
2-Aminophenol	2,5	93	0,28	0,021	50,5
4-Aminophenol	2,5	98	0,29	0,006	52,1
2-Benzylidenaminophenol	4,0	98	0,29	0,012	136,9
4-Benzylidenaminophenol	4,0	96	0,29	0,012	131,5
Catalyst Li[AlCl$_4$]					
4-iso-Propylphenol	2,5	91	0,27	0,023	-
1,3-di-Oxybenzene	2,0	95	0,28	0,015	-
Catalyst K[AlCl$_4$]					
4-iso-Propylphenol	2,5	93	0,28	0,021	-
1,3-di-Oxybenzene	2,0	96	0,58	0,012	-
Polypropylene					
Catalyst Na[AlCl$_4$]					
Phenol	2,5	96	0,89	0,037	141,3
2-Methylphenol	2,5	94	0,87	0,056	141,0
3-Methylphenol	3,0	90	0,84	0,093	140,5
4-iso-Propylphenol	3,0	94	0,87	0,056	135,3
2,6-di-Tertbutylphenol	4,0	87	0,81	0,121	140,9
1,2-di-Oxybenzene	2,5	92	1,71	0,074	154,7
1,3-di-Oxybenzene	2,5	98	1,82	0,019	128,5
1,4-di-Oxybenzene	2,5	89	1,65	0,010	137,3
2-Aminophenol	2,5	93	0,86	0,065	58,6

TABLE I (*Continued*)

Phenol	Reaction time, hr	Product yield, %	HO-group content, mol/mol polyolefinylphenol	$>C=C<$ bond content, mol/mol polyolefinylphenol	^{13}C NMR-spectra, δ, m.d. (signal of C, linked with the oligomer radical)
1	2	3	4	5	6
4-Aminophenol	2,5	97	0,90	0,028	57,0
2-Benzylidenaminophenol	4,0	98	0,91	0,028	142,6
4-Benzylidenaminophenol	4,0	94	0,87	0,056	137,2
	Polyisobutylene Catalyst $Na[AlCl_4]$				
Phenol	2,5	98	0,98	0,020	143,5
2-Methylphenol	2,5	95	0,95	0,050	143,1
3-Methylphenol	3,0	91	0,91	0,090	142,7
4-iso-Propylphenol	3,0	96	0,96	0,040	137,5
2,6-di-Tertbutylphenol	4,0	85	0,85	0,150	143,1
1,2-di-Oxybenzene	2,5	94	1,88	0,060	156,9
1,3-di-Oxybenzene	2,5	98	1,96	0,020	130,7
1,4-di-Oxybenzene	2,5	91	1,82	0,090	139,5
2-Aminophenol	2,5	90	0,90	0,100	54,1
4-Aminophenol	2,5	95	0,95	0,050	55,9
2-Benzylidenaminophenol	4,0	98	0,98	0,020	144,8
	EPR Catalyst $Na[AlCl_4]$				
2,6-di-Tertbutylphenol	6,0	82	0,37	0,081	135,2
1,2-di-Oxybenzene	5,0	84	0,76	0,072	136,8
1,3-di-Oxybenzene	5,0	85	0,77	0,070	125,6
2-Aminophenol	4,0	84	0,38	0,078	57,7
2-Benzylidenaminophenol	6,0	84	0,38	0,072	139,7
4-Benzylidenaminophenol	6,0	83	0,37	0,077	134,4
	EPRT Catalyst $Na[ALCl_4]$				
2-Methylphenol	5,0	80	1,87	0,470	138,1
2,6-di-Tertbutylphenol	6,0	79	1,85	0,492	139,1
1,2-di-Oxybenzene	5,0	85	3,98	0,351	141,7

TABLE I (*Continued*)

Phenol	Reaction time, hr	Product yield %	HO-group content, mol/mol polyolefinylphenol	$>C=C<$ bond content, mol/mol polyolefinylphenol	^{13}C NMR-spectra, δ, m.d. (signal of C, linked with the oligomer radical)
1	2	3	4	5	6
		Oligopiperilene			
		Catalyst $Na[AlCl_4]$			
4-iso-Propylbenzene	4,0	76	6,08	1,920	135,6
1,4-di-Oxybenzene	4,0	84	13,44	1,280	137,9
1,2-di-Oxybenzene	4,0	85	13,60	1,200	142,3
4-Aminophenol	4,0	82	6,56	1,440	51,1
4-Benzylidenaminophenol	5,0	80	6,40	1,600	136,5

TABLE II

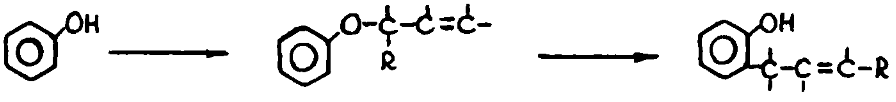
The effect of the oligomer radical length in oligoisobutylenylphenols on the HAO output and the dehydrochlorination rate of chlorine-containing rubbers ($c = 2\cdot10^{-2}$ AO mol/polymer kG, 423 K, air)

Compound	M_p oligoisobutylenylphenols	Yield, mass%	Dehydrochlorination rate, $\mathcal{V}_{HCL}\cdot10^{-7}$mol HCL/CL mol in polymer·s	
			CPE	CPER
2,6-di-tertbutyl-4-oligoisobutylenylphenol	720	98	4,6	7,3
	880	97	4,5	7,4
	1100	97	4,6	7,5
	1500	96	4,4	7,3
	3500	95	4,5	7,5
4-oligoisobutylenyl-1,2-dioxybezene	720	98	4,1	7,0
	880	98	4,2	7,1
	1100	97	4,1	7,1
	1500	95	4,2	7,0
	3500	91	4,1	7,2
2,6-di-tertbutylphenol			6,4	8,7
1,2-dioxybenzene			6,2	8,6
without AO			8,3	14,2

Thus, the alkylation of phenols and aminophenols in the presence of $\mathrm{Me[AlCl_4]}$ is a viable method for the synthesis of high-molecular phenols. The process runs easily under mild experimental conditions and is not accompanied by the formation of side products.

Introducing phenolic fragments into a polymer chain opens wide prospects for their subsequent polymer-analogous conversions.

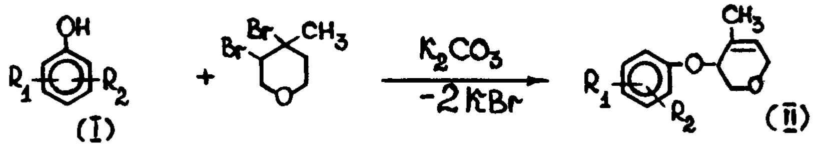
Numerous examples of the synthesis of various phenol derivatives using the Claisen rearrangement are described in Reference 11.


(4)

The original way of synthesis and rearrangement of phenyl ethers of 5,6-dihydro-2H-pyrans is given in Reference 12. Unlike low-molecular phenols, chemical reactions with high-molecular ones are not sufficiently investigated. The data concerning the Claisen rearrangement are based upon exceptionally low-molecular compounds.

Therefore it was really interesting to study the synthesis and rearrangements of high-molecular phenyl ethers.

The synthesis of phenol ethers (II) has been carried out according to Reference 12 by heating high-molecular phenols (I) with 3,4-dibrome-4-methyltetrahydropyran (dibromide) in the hexane medium catalysed by K_2CO_3:


(5)

where a) $R_1 = H$, $R_2 = \mathrm{4{-}H({-}CH_2{-}CH_2{-})_m\overset{|}{C}H{-}CH_2({-}CH_2{-}CH_2{-})_1}$, $m + l = n - 1 = 53$ (PE); b) $R_1 = \mathrm{2{-}CH_3}$, $R_2 = \mathrm{4{-}PE}$; c) $R_1 = \mathrm{4\text{-}}i\mathrm{\text{-}C_3H_7}$, $R_2 = \mathrm{2{-}PE}$; d) $R_1 = \mathrm{2{-}N{=}CHC_6H_5}$, $R_2 = \mathrm{4{-}PE}$; e) $R_1 = \mathrm{4{-}N{=}CHC_6H_5}$, $R_2 = \mathrm{2{-}PE}$; f) $R_1 = H$, $R_2 = \mathrm{4{-}H({-}CH_2{-}\underset{CH_3}{\underset{|}{C}}H{-})_m{-}CH_2{-}\overset{|}{\underset{CH_3}{\underset{|}{C}}}{-}({-}CH_2{-}\underset{CH_3}{\underset{|}{C}}H{-})H}$, $m + l = n - 1 = 33$ (PP); g) $R_1 = \mathrm{2{-}CH_3}$, $R_2 = \mathrm{4{-}PP}$; h) $R_1 = \mathrm{4{-}}i\mathrm{{-}C_3H_7}$, $R_2 = \mathrm{2{-}PP}$; i) $R_1 = \mathrm{2{-}N{=}CHC_6H_5}$, $R_2 = \mathrm{4{-}PP}$; j) $R_1 = \mathrm{4{-}N{=}CHC_6H_5}$, $R_2 = \mathrm{2{-}PP}$; l) $R_1 = H$, $R_2 = \mathrm{4{-}H({-}CH_2{-}\overset{CH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-})^3}\ n - 1$

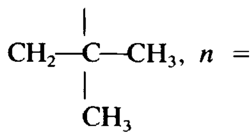
TABLE III

The characteristics of high-molecular monohydric phenols, benzylidenaminophenols and their rearrangement products

Letter index of compounds *	Condensation (compounds II)		Rearrangement (compounds III)	
	Product yield, mass %	$^{13}C, \delta$**, m.d.	HO-group content mol/polyolefinylphenol mol	$^{13}C, \delta$**, m.d.
a	96,4	140,7	0,29	136,9
b	92,9	140,5	0,28	136,6
c	91,5	136,0	0,28	130,2
d	92,6	142,0	0,29	138,2
e	91,3	137,9	0,29	132,8
f	95,0	146,4	0,89	142,6
g	93,1	146,3	0,87	142,4
h	92,2	141,7	0,87	136,6
i	93,0	147,7	0,91	143,9
j	91,4	143,6	0,87	138,5
l	96,1	148,6	0,98	144,8
m	96,0	148,3	0,95	144,6
n	91,8	143,9	0,96	138,8
o	90,9	149,9	0,98	145,8
p	90,1	153,5	0,94	140,7

* The letter index relates to the compounds with the corresponding index in the explanation to the schemes of reactions (5) and (6)

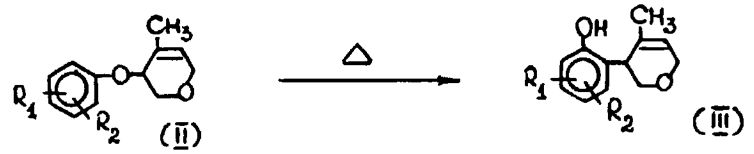
** C- atom signal, linked to the polymer fragment.



$CH_2-\underset{CH_3}{\overset{|}{C}}-CH_3$, $n = 19$ (PIB); m) $R_1 = 2-CH_3$, $R_2 = 4-$(PIB); n) $R_1 = 4-i-C_3H_7$, $R_2 = 2-$PIB; o) $R_1 = 2-N{=}CHC_6H_5$, $R_2 = 4-$PIB; p) $R_1 = 4-N = CHC_6H_5$, $R_2 = 2-$PIB.

The yield of phenol ethers of dehydropyran type (compounds IIa–IIp) ranged from 90 to 96%, i.e. was close to being quantitative (Table III) while for the low-molecular ethers the yield value did not exceed 65–67%.[12]

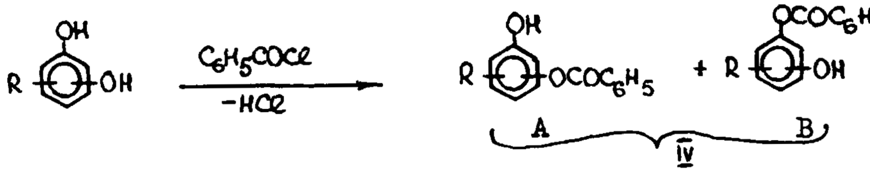
In boiling phenyl ethers IIa–IIp in N,N-diethylaniline (170°C, 6 hr) the compounds with the quantitative yield were transformed into corresponding high-molecular phenols of dihydropyran row with the formation of ortho-isomers.



(6)

The structure of compounds (II)–(III) has been tested by spectral and chemical methods. In the ^{13}C NMR-spectra of compounds IIa–IIp there is a signal of the aromatic ring carbon, linked to the pyran ring; in the IR-spectra there are two absorption bands at 1060 – 1080 cm^{-1} and 1220 cm^{-1}, caused by the vibrations of two ether bonds C—O—C. In the IR-spectra of compounds IIIa–IIIp there is an intense band of the HO-group in the range of 3000–3600 cm^{-1}. The analytical control of HO-groups according to Verley[13] shows their absolute absence in products II. The content of HO-groups in compounds III corresponds to their amount in the starting high-molecular phenols (Table III).

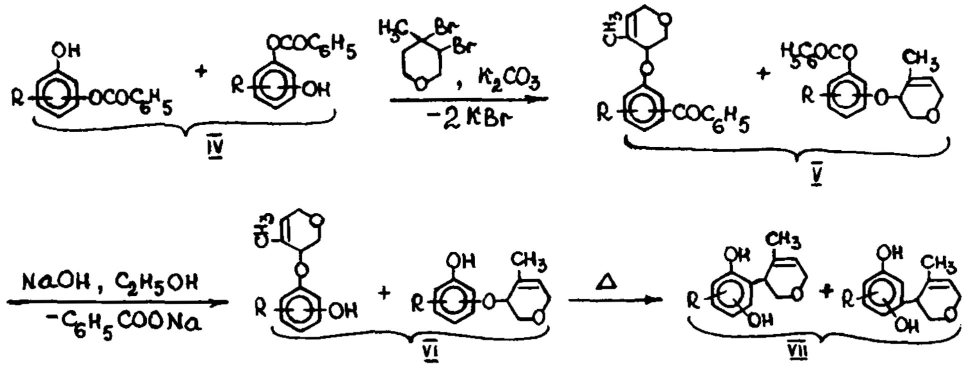
For dihydric phenols the production of monoethers with the quantitative yield is possible only under the condition of the preliminary protection of one of the HO—group, for instance, by benzoylation:



(7)

IV. a) 2—OH, R = 4PIB; b) 3—OH, R = 4—PIB; c) 4—OH, R = 2—PIB; d) 2—OH, R = 4—PP; e) 3—OH, R = 4—PP; f) 4—OH, R = 2PP; g) 2—OH, R = 4—PE; h) 3—OH, R = 4—PE; i) 4—OH, R = 2—PE.

The presence of two hydroxy-groups in the initial high-molecular phenols is responsible for the appearance of two isomers (for instance, in case of catechol: of 2-benzoyl-4-oligoolefinylphenol (A) and 2-benzoyl-5-oligoolefinylphenol (B)) in benzoylation products IV. This results in a mixture of isomeric products on condensing compounds IV with the subsequent Claisen rearrangement. Polymer-analogous reactions of benzoylated phenols have been carried out according to the scheme:



(8)

The condensation of compounds IV with dibromide has been conducted in a similar way than that of monohydric phenols. The reaction proceeded easier (the reaction time for compounds Ia–IIp = 24 hrs, compounds IVa–IVi = 12 hrs). This is associated with the presence of the —$OCOC_6H_5$-group in the aromatic ring exhibiting a negative M-effect and promoting the hydroxy-group protone detachment and contributing to the condensation.

The hydrolysis of compounds V in the water-alcohol solution of NaOH caused the formation of products VI. The Claisen rearrangement of compounds VI ran without difficulties with the yields comparable to those of high-molecular monohydric phenols (Table IV).

TABLE IV

The characteristics of compounds IV-VII

The letter index of compounds *	Benzoylation (compounds IV)			Condensation (compounds V)		Hydrolysis (compounds VI)			Rearrangement (compounds VII) ***	
	Yield, %	The HO-group content, mol//mol of initial polymer phenol	^{13}C, δ **, m.d.	Yield, %	^{13}C, δ **, m.d.	Yield, %	The HO-group content, mol/product mol	^{13}C, δ **, m.d.	The HO-group content, mol/product mol	^{13}C, δ **, m.d.
a	98,5	2,80	$\frac{144,9}{150,2}$	89,0	$\frac{149,8}{149,5}$	99,1	1,40	$\frac{150,2}{139,5}$	2,80	$\frac{146,2}{133,2}$
b	99,0	2,80	$\frac{135,9}{137,2}$	91,0	$\frac{142,2}{142,6}$	95,3	1,40	$\frac{130,9}{135,8}$	2,80	$\frac{132,0}{132,9}$
c	98,4	2,80	$\frac{139,4}{145,9}$	88,2	$\frac{145,8}{145,3}$	98,3	1,40	$\frac{150,1}{139,4}$	2,80	$\frac{147,2}{137,3}$
d	98,0	2,30	$\frac{142,7}{143,6}$	88,1	$\frac{147,7}{143,9}$	96,1	1,15	$\frac{147,4}{137,3}$	2,30	$\frac{138,7}{135,1}$
e	99,0	2,16	$\frac{133,7}{135,4}$	90,1	$\frac{140,0}{140,2}$	98,4	1,08	$\frac{135,0}{133,7}$	2,16	$\frac{130,2}{129,7}$
f	98,5	2,18	$\frac{137,3}{142,7}$	89,3	$\frac{143,6}{144,1}$	99,0	1,09	$\frac{142,0}{137,4}$	2,18	$\frac{138,8}{135,1}$
g	98,8	0,58	$\frac{137,0}{142,0}$	90,2	$\frac{142,1}{141,9}$	98,2	0,29	$\frac{141,8}{137,1}$	0,58	$\frac{133,0}{130,6}$
h	98,4	0,56	$\frac{128,0}{129,5}$	91,8	$\frac{134,3}{134,6}$	99,5	0,28	$\frac{129,3}{128,1}$	0,56	$\frac{124,3}{125,0}$
i	98,4	0,56	$\frac{131,6}{138,0}$	91,9	$\frac{137,9}{137,6}$	97,9	0,28	$\frac{138,2}{131,7}$	0,56	$\frac{133,3}{129,4}$

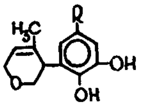
* The letter indeces relate to the compounds, obtained in reactions (7) and (8)

** Numerator - the ralue for the "A" isomer, denominator - for the "B" isomer

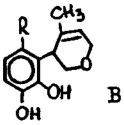
*** The quantitative yield.

The structure of compounds IV–VII has been tested by spectral and chemical methods. The structure of benzoylated products IV was established by the ^{13}C-NMR spectra. The Table IV gives the values of the chemical shift of the singlet signal of the carbon atom linked to the oligomer radical. The quantitative determination of the HO-group content reflects the shielding of one group only. In condensation products V the absence of the HO-groups was determined by the chemical analysis and the IR-spectra data. After the hydrolysis of compounds V the intense absorption band in the range of 3300–3600 cm^{-1} appears again in the IR-spectra. The analysis has revealed the appearance of one hydroxy-group in compounds VI and two hydroxy-groups in compounds VII.

To establish the ratio of isomers in the condensation products on the basis of different high-molecular phenols, the results of chromatography and the data of the ^{13}C NMR-spectroscopy of the products of a model reaction-the reaction of 4-methyldioxybenzenes (low-molecular analogue) with dibromide were used. The following ratios of isomers have been found: 3-(4-methyl-5,6-dihydro-2H-pyranyl)-5-methyl-1,2-dioxybenzene and 3-(4-methyl-5,6-dihydro-2H-pyranyl)-4-methyl-1,2-dioxybenzene—1:1; 2-(4-methyl-5,6-dihydro-2H-pyranyl)-4-methyl-1,3-dioxybenzene and 4-(4-methyl-5,6-dihydro-2H-pyranyl)-6-methyl-1,3-dioxybenzene—3:1; 3-(4-methyl-5,6-dihydro-2H-pyranyl)-5-methyl-1,4-dioxybenzene and 2-(4-methyl-5,6-dihydro-2H-pyranyl)-5-methyl-1,4-dioxybenzene—3:1. The given ratios are most likely to be the same in transforming methyl radical into the oligomer one, i.e. for the isomeric products synthesized on the basis of polymer-analogous conversions involving high-molecular catechol there exists the ratio of isomers A:B = 1:1, and for the products, obtained on the basis of high-molecular resorcinol and hydroquinone there is a ratio A:B = 3:1.

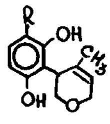


A

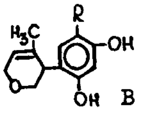


B

for catechol

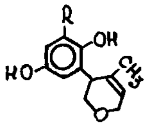


A

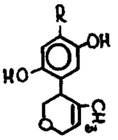


B

for resorcinol



A



B

for hydroquinone

Therefore, the possibility of synthesis of phenyl ethers and their subsequent Claisen rearrangement has been shown for different high-molecular mono- and dihydric phenols. The introduction of a macroradical into the aromatic ring contributes to the completion of the reaction and considerably increases the yield of the synthesized products in comparison with the low-molecular analogue.

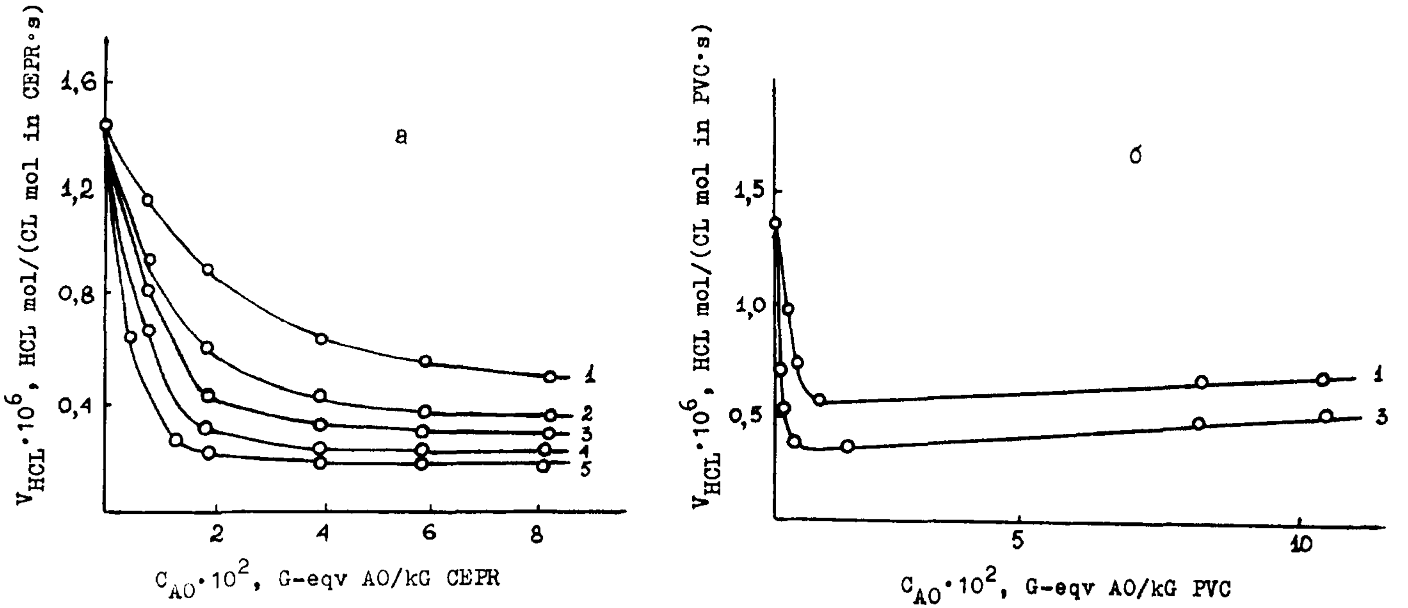


FIGURE 1 The dependence of the dehydrochlorination rate of CEPR (a) and PVC (b) on the phenolic AO concentration. 1. 1,2-di-oxybenzene; 2. 4-methyl-2,6-di-tertbutylphenol; 3. 4-oligoisobutylenyl-1,2-di-oxybenzene; 4. 4-oligopiperilenyl-1,2-di-oxibenzene; 5. 2-oligopiperilenyl-1,4-di-oxybenzene.

The synthesized compounds possess the properties of polyfunctional chemical additives for a number of chlorine-containing polymers (chlorinated ethylene-propylene rubber—CEPR, chlorine ethylene-propylene ternary rubber—CEPTR, chlorosulfopolyethylene—CSPE, chlorinated polyethylene—CPE, vinyl chloride polymer—PVC). They retard the polymer dehydrochlorination rate, improve the thermal stability and color fastness of the products and facilitate the processing of stiff PVC.

The stabilizing effect of HAO in some formulations exceeds that of the corresponding low-molecular analogues.

The kinetic curves of the dehydrochlorination of CEPR and PVC in the presence of oligoisobutylenyl- and oligopiperylenylphenols (compounds I) and their low-molecular analogues are given in Figure 1. HAO reduces the rate of the CEPR dehydrochlorination to a greater extent than the corresponding low-molecular analogues and the industrial AO—4-methyl-2,6-di-tertbutylphenol; in the oxidizing media the HAO decrease the HCL-elimination rate by a factor of 2.5–3.0 while the corresponding low-molecular phenols only by a factor of 1.5.

The study of the kinetics of CEPR and CPE dehydrochlorination in the presence of oligoisobutylenylphenols of various molecular mass (720 + 3500) has shown that the HAO effectivity is independent of the oligomer radical length (Table II). Obviously, the macroradical length within these limits does not influence the HAO mobility in chlorine-containing synthetic rubbers that determine their homogeneous distribution in the protected polymer.[2]

The dependence of the PVC dehydrochlorination rate on the concentration of high-molecular dihydric phenols is somewhat different from that of CEPR (Figure 1b).

The introduction of dihydric phenols reduces the PVC dehydrochlorination rate, but when the concentration exceeds $1 \cdot 10^{-3}$ HO-eqv/kG of PVC the elimination rate rises again. Therefore, dihydric phenols exhibit a critical concentration above which the polymer degradation rate is increased. The analogous dependences have been observed earlier[14] in PVC dehydrochlorination in the presence of 4-methyl-2,6-di-tert-butylphenol and diphenylolpropane. As in the case with CEPR, the HAO exerts greater inhibiting effect on the HCL-elimination rate, than its low-molecular analogues.

The character of kinetic curves of dehydrochlorination of PVC and CEPR is retained when other phenolic HAO (oligoethylenylphenol, oligopropylenylphenol, phenols, alkylated EPR and CEPTR) are used.

The stabilizing effect of the HAO depends on the chemical composition of both the phenol and the oligomer radical. For the same oligomer radical it increases when passing from monohydric phenols to the dihydric ones, and for the phenols of the same type it increases in the following order: oligoethylenylphenol < phenol, alkylated EPR < oligopropylenylphenol < phenol, alkylated CEPTR < oligopiperylenylphenol, i.e. with the increase of number of phenolic fragments in the HAO (Table V).

Alkylated aminophenol oligomers are not more effective stabilizers than their low-molecular analogues (Figure 2a). However, the simultaneous introduction of 4-benzylidenamino-2-oligopiperilenylphenol and 4-oligopiperilenylaminophenol the

TABLE V

The dependence of HAO efficiency on the nature of phenol and oligomer radical ($C = 2 \cdot 10^{-2}$ HAO mol/polymer kG, 423 K, air)

HAO	HO-content group mol/mol	The dehydrochlorination rate $V_{HCL} \cdot 10^7$ mol HCL/(CL mol in polymer·s)	
		CPE	CEPRT
2,6-di-Tertbutyl-4-oligoethylenylphenol	0,27	6,0	10,8
2,6-di-Tertbutylphenol, alkylated by EPR	0,37	5,7	9,7
2,6-di-Tertbutyl-4-oligopropylenylphenol	0,81	5,0	8,4
2,6-di-Tertbutyl-4-oligoisobutyllenylphenol	0,85	4,6	8,1
2,6-di-Tertbutylphenol, alkylated by EPRT	1,85	4,2	6,7
2,6-di-Tertbutyl-4-oligopiperilenylphenol	6,32	3,2	5,4
4-Oligoethylenyl-1,2-dioxybenzene	0,56	5,6	9,8
1,2-di-Oxybenzene, alkylated by EPR	0,76	5,4	9,1
4-Oligopropylenyl-1,2-dioxybenzene	1,71	4,6	8,0
4-Oligoisobutylenyl-1,2-di-oxybenzene	1,88	4,2	7,8
1,2-di-oxybenzene, alkylated by EPRT	3,98	3,6	6,7
4-Oligopiperilenyl-1,2-di-oxybenzene	13,60	2,9	5,0
Without AO		8,3	15,5

synergetic phenomenon in the "dehydrochlorination rate" is observed (Figure 2b, Table VI). This phenomenon has not been observed in the case of the low-molecular analogues.

The kinetic curves of the CEPTR and CPE dehydrochlorination in the presence of the oligomer-alkylated α-olefins and dienes of phenols and aminophenols was not essentially different from the corresponding dependences for CEPR.

The HAO-stabilized samples of chlorine-containing polymers preserve their color and elasticity during 10–12 hr of degradation while for the low-molecular AO the irreversible color change is observed accompanied by film cracking as early as in 3.5 ± 0.5 hrs. The introduction of the pyranyl radical into an aromatic ring of high-molecular phenols (compounds III and VII) contributes to the greater effi-

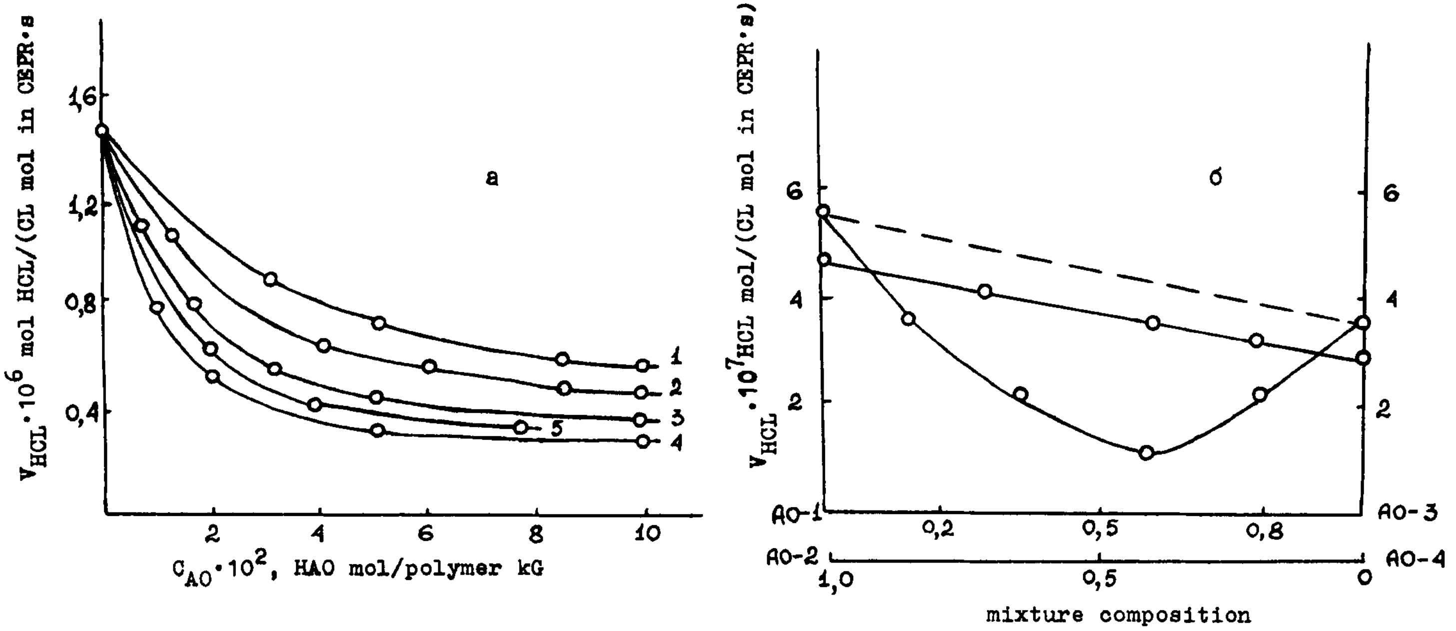


FIGURE 2 The dependence of the dehydrochlorination rate of CEPR on the concentration of the aminophenolic AO (a) and on the individual component ratio in the aminophenolic AO blend (b). a) 1. 4-benzylidenamino-2-oligoperilenylphenol; 2. 4-benzylidenaminophenol; 3. 4-oligopiperilenylaminophenol; 4-aminophenol; 5. 4-methyl-2,6-di-tertbutylphenol. b) mixture of 1 and 3; 2. mixture of 2 and 4 (see Figure 2 a for the designation). The sum concentration of AO is $6 \cdot 10^{-2}$ mol AO/polymer kG.

TABLE VI

The rates of thermooxidative dehydrochlorination of halogen-containing polymers in the presence of aminophenols (423 K, air)

AO C= $6\cdot10^{-2}$ AO mol/polymer kG	Dehydrochlorination rate $V_{HCL}\cdot10^{7}$ HCL mol/CL mol in polymer·s)	
	CPE	CEPR
1. 4-aminophenol	1,9	3,2
2. 4-benzylidenaminophenol	2,8	4,8
3. 4-oligopiperilenylaminophenol	1,9	3,3
4. 4-benzylidenamino-2-oligopiperilenylphenol	3,8	6,5
5. sinergetic blend (3 and 4)	0,8	1,2
6. 4-methyl-2,6-di-tertbutylphenol	2,1	3,6
7. without AO	8,3	14,2

ciency of HAO in "thermal stability length" and "color fastness." The data on thermal stability and color fastness of chlorine-containing polymers (448 K) are summarized in Tables VII and VIII.

Oligoisobutylene-alkylated phenols considerably improve the processing the stiff PVC and increase the polymer melt index (Figure 3). In this case the lubricating effect of the additive increase as the hydrocarbon radical lengthens and it does not depend on the nature (mono- or dihydric one) of phenol. The introduction of the pyranyl radical into the phenol ring leads to the significant growth of the polymer melt index.

Thus, the products of the polymer-analogous reactions of oligomers of α-olefins and piperilene with phenols turn out to be effective complex stabilizers for chlorine-containing polymers. They reduce the HCL-elimination rate, improve the color and elasticity of the films, facilitate the PVC processing. The HAO are compatible with the protected polymers, are not extracted by water, and do not volatilize at higher temperatures and in vacuum.

The synthesis of HAO using non-standard oligomer or side (oligopiperylene) products of the large-scale polymer production is especially interesting because three tasks are solved simultaneously: 1) the utilization of the waste of different polymer industries (the problem, which is of great importance both from ecological and commercial points of view), 2) the synthesis of new useful products, and 3) the lower cost of the obtained stabilizers. This makes the alkylation of α-olefins and dienes of different phenols and aminophenols using oligomers a very promising way for synthesizing new complex chemical additives for halogen-containing polymers.

TABLE VII

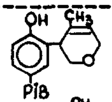
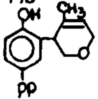
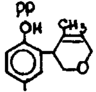
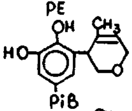
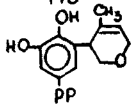
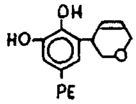
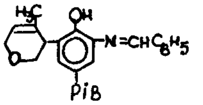
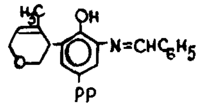
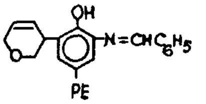
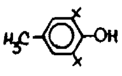
The effect HAO on thermal- and color stability of halogen-containing polymers (448 K, air, C_{HAO} = 1 m.p.)

HAO	PVC	CPE	CEPR	CEPRT
1	2	3	4	5
4-Oligoethylenylphenol	33/3,5	29/3,0	27/2,5	23/3,0
2-Methyl-4-oligopropylenylphenol	38/3,0	-	32/3,0	-
4-iso-Propyl-2-oligopropylenylphenol	-	33/3,0	-	29/3,0
	34/3,5	30/3,0	29/3,0	25/3,5
3-Methyl-4-oligoisobutylenylphenol	41/3,0	35/3,0	33/3,0	30/3,0
2-Methylphenol, alkylated by EPRT	45/3,0	39/3,0	35/3,0	34/3,5
4-iso-Propyl-2-oligopiperilenylphenol	54/3,0	50/2,5	46/2,0	37/2,5
1,3-di-Oxybenzene, alkylated by EPR	49/2,0	45/2,5	40/2,5	37/3,0
4-Oligoisobutylenyl-1,3-dioxybenzene	53/2,0	-	45/1,5	35/2,5
1,4-di-Oxybenzene, alkylated by EPRT	56/2,0	50/2,0	48/1,5	37/2,0
2-Oligopiperilenyl-1,4-dioxybenzene	65/2,5	60/2,5	55/2,0	44/2,5
2-Oligoethylenylaminophenol	-	-	40/3,5	-
4-Oligopropylenylphenol	-	42/3,5	-	37/3,5
2-Aminophenol, alkylated by EPR	-	-	42/3,5	39/3,5
4-Oligopiperilenylaminophenol	-	56/3,5	50/3,5	41/4,0
2-Benzylidenaminophenol, alkylated by EPR	33/3,5	30/3,0	28/2,5	-
2-Benzylidenamino-4-oligo-iso-butylenylphenol	40/3,0	35/3,0	33/3,0	-
4-Benzylidenaminophenol, alkylated by EPRT	-	40/3,0	-	29/3,0
4-Benzylidenamino-2-oligopiperilenylphenol	52/3,0	48/2,5	45/3,0	35/3,0
The synergetic blend of 4-benzylidenamino-2-oligopiperilenylphenol with 4-oligopiperilenylaminophenol	-	91/3,5	85/3,5	77/4,0
2,6-di-Tertbutyl-4-methylphenol	20/4,5	24/4,5	20/4,5	18/5,0
Without AO	3/6,0	7/5,0	3/5,0	2/6,5

* Numerator - the duration of thermal stability τ, min; denominator - color fastness, "Synmero" scale points.

TABLE VIII

The effect of high-molecular pyranylphenols on thermal stability and color fastness of halogen-containing polymers (448 K, air) C_0 = 1 m.p.*

Compound	PVC τ,min / colour, points	CPE τ,min / colour, points	CEPR τ,min / colour, points	CSPE τ,min / colour, points
	54/1,5	58/1,5	-	47/1,5
	51/1,5	44/1,5	-	34/2,5
	48/2,0	49/1,0	-	38/2,0
	79/1,5	61/1,5	-	51/1,5
	75/1,5	59/1,5	-	42/2,0
	69/1,5	51/1,5	-	42/2,0
	43/2,0	-	33/2,5	29/2,5
	41/2,0	-	31/2,5	27/2,5
	39/2,0	-	28/2,5	25/3,0
	20/4,5	24/4,5	20/4,5	17/5,0

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*numerator - the duration of thermal stability, min; denominator - colour fastness, according to the Synmero scale.

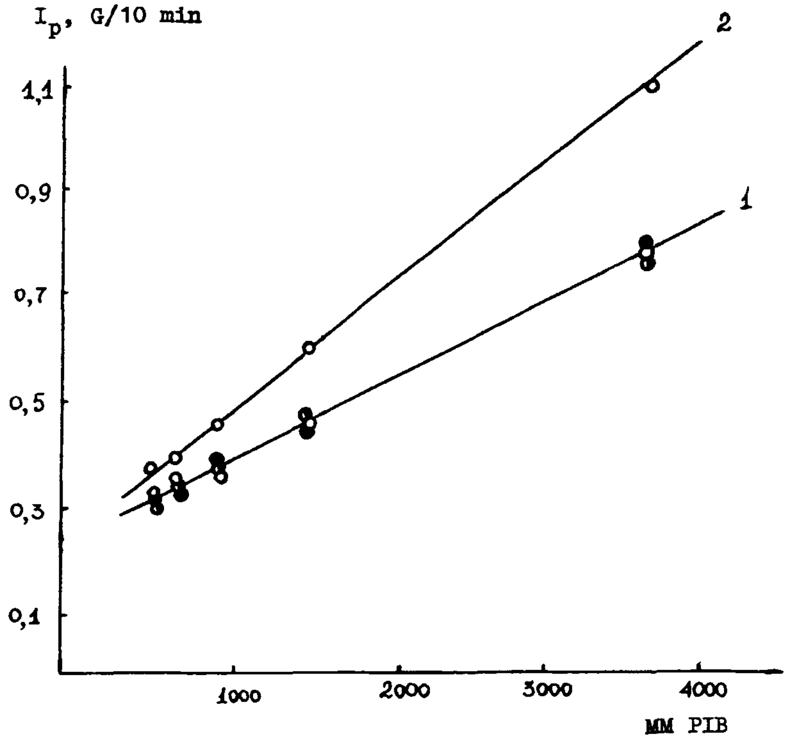

FIGURE 3 The dependence of the melt index of stiff PVC-compositions on the molecular mass (*M*) of oligoisobutylenylphenols 1. 2,6-di-tertbutyl-4-oligoisobutylenylphenol (○), 3-oligo-isobutyllenyl-1,4-di-oxibenzene (◑) and 4-oligoisobutylenyl-1,2-di-oxybenzene (●); 2. 2-(4-methyl-5,6-dihydro-2H-pyranyl)-4-oligoisobutylenylphenol.

THE EXPERIMENTAL PART

The Synthesis of Compounds I

The alkylation of mono- and dihydric phenols and aminophenol using oligomers of α-olefins and piperilene was carried out in saturated hydrocarbon medium at 393 ± 20 K during 2 + 6 hr depending on the nature of oligomer and phenol. The complex salt Me[$AlCl_4$], where Me = Li, Na, K was used as a catalyst. The molar ratio of oligomer to:phenol to:catalyst is 1:1:0.05. The extent of the reaction proceeding was controlled with ozonometry by the reduction of the double bond content in the oligomer as compared to the initial sample and by the number of hydroxy-groups, contained in the polymer chain (titration by Verley[13]). The yield of HAO was 75–85% for oligopiperylenylphenols and copolymers of ethylene and propylene (EPR and EPTR) and more than 90% for oligomers of ethylene, propylene and isobutylene.

Oligopiperylene-based HAO represented light-yellow odorless powders, HAO on the basis of other oligomers were highly viscous gel-like products, colorless or slightly colored (yellowish-beige) depending on the phenol nature. The products of the synthesis are easily soluble in aliphatic and aromatic hydrocarbons, in CCl_4, and are not soluble in the polar solvents (water, alcohol, acetone). For the HAO synthesis we used: oligopiperylene $\bar{M}_n = 1200–1500$ with eight $>C=C<$ bonds in a molecule; oligoisobutylene $\bar{M}_n = 720 + 3500$, containing one $>C=C<$ bond at the end of the chain (the degree of unsaturation is 1.00); oligoethylene $\bar{M}_n = 1300$, the degree of unsaturation is 0.30; oligopropylene $\bar{M}_n = 1400$, the degree of unsaturation 0.93; EPR—viscosity by Muni is 60 (373 K), the propylene content is 38 mass %; the degree of unsaturation is 0.45; EPTR—the third monomer—dicyclopentadiene is 1.52 mass %, the degree of unsaturation 2.34.

The Synthesis of Compounds II and V

$1 \cdot 10^{-2}$ Mol of oligo-α-olefinylphenol (compounds I) or $9.84 \cdot 10^{-3}$ mol of benzoylated oligo-α-olefinyldioxybenzenes (compounds IV) were dissolved in 200 ml of hexane, $2.9 \cdot 10^{-3}$ ($9.84 \cdot 10^{-3}$) mol of 3,4-dibrom-4-methyltetrahydropyrane, $0.87 \cdot 10^{-2}$ ($2.95 \cdot 10^{-2}$) mol of potassium carbonate were added and heated for 24 (12)‡ hrs. After cooling down the reaction mixture was filtered, the filtrate was washed first with water, then with alcohol. The yield is summarized in Tables III and IV.

The Synthesis of Compounds III and VII

Compounds II and VI were dissolved in N,N-diethylanilyne ($7.8 \cdot 10^{-3}$ mol in 80 ml) and were heated for 6 (5)‡ hr on a water bath. After cooling down N,N-diethylaniline was removed from the reaction mixture in vacuum, the residue was dissolved in hexane and the synthesis products were precipitated with alcohol. The yield is quantitative.

The Synthesis of Compounds IV

10% Solution of NaOH ($1 \cdot 10^{-2}$ mol) was added to $1 \cdot 10^{-2}$ mol of oligo-α-olefinyl-1,2-dioxybenzene, the mixture was stirred for 30 minutes, then $1 \cdot 10^{-2}$ mol of chlorine benzoyle was added by drops and heated for 30 minutes on a water bath with intense stirring. The amounts of chlorobenzoyl and NaOH were calculated in such a way that only half of the oxy-groups were protected.

The Synthesis of Compounds VI

80 Ml of water-alcohol solution of NaOH ($6.5 \cdot 10^{-3}$ mol) were added to $6.4 \cdot 10^{-3}$ mol of compounds V and heated on a water bath for 6 hr. The product was washed with water and alcohol. The yield of products V, VI is summarized in Table IV.

The IR-spectra were made by the spectrometer "Specord MK-80" in the CCl_4 solution, the ^{13}C NMR-spectra—by the Bruker AM-350 (75 MHz) spectrometer

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‡Conditions of synthesis of compounds V and VII.

at the room temperature in the regime of full and partial suppression of protones. The conditions of recording were 15–20% solutions in $CDCl_3$, the pulse periods is of 3–5 s, the accumulation number of 3000–10,000, the inner standard of TMS.

The ozonometric determination of the degree of unsaturation was carried out using the ADC-4M device; the solvent was CCl_4, the inner standard stilbene.

The conditions of gas chromatography: a 50 m long quartz capillary column with the inner diameter of 0.25 mm, nonpolar mobile phase—OV-1; gass carrier—helium, 1.0–1.5 cm³/min, by-pass—100 cm³/min; the temperature programmed—from 70 to 250°C, 6°/min, the sample volume—0.2 mcl; the quantitative calculation of the chromatograms was made by the inner normalization method.

The degradation of chlorinated rubber films having a thickness of $(1.9 + 2.5)\cdot 10^{-5}$ m and PVC powder was carried out in a U-form reactor. The eliminated HCl was blown out with the air current (thermoxidative destruction) or with the purified nitrogen (thermal destruction). HCl was absorbed in distilled water and was quantitatively determined by titration. HAO was introduced into polymers in the form of chloroformic solutions. The relative error in the determination of dehydrochlorination rate did not exceed 5% for the confidence level of 0.90. The thermal stability duration τ(min) was determined by the time when a "congored" placed under the polymer started turning blue. The color fastness was determined by comparing the color of the polymer at the moment τ with the 10-point color scale "Synmero" (the white color corresponds to the black one—to 10). The PVC melt index (the amount of polymer (G), flowing out from the capillary tube for the time of 10 min) was determined using the MV-3M viscosimeter (loading $P = 2.580$ kG, the capillary diameter $d = (2.08\text{–}2.10)\cdot 10^{-3}$ m, $T = 463$ K).

The specimens used in the study were; CEPR with the chlorine content of 25.6%, CEPTR with the chlorine content of 11.7 mass %, CPE with the chlorine content of 28.7 mass %, obtained by chlorination of EPR, EPTR respectively (the third monomer—dicyclopentadiene—1.52 mass %) with HPPE ($\bar{M}_n = 20{,}000$) in CCl_4 at 333 K, and the industrial sample of PVC of C-70 grade and CSPE with the chlorine content of 29.5% and sulfur content of 1.4 mass %. The CSPE sample was obtained from polyethylene with the molecular mass of 20,000.

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