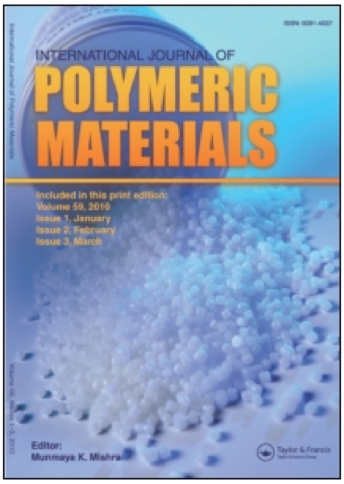

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Functionalization of Olefin and Diene Oligomers by Oxygen-, Nitrogen-, Phosphorus- and Silicon-Containing Compounds

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Functionalization of non-polar oligomers of olefins and cycles by phenols and aminophenols with their further polymer-analogous transformations under soft experimental conditions is studied. The substances synthesized are chemicals-additives of polyfunctional action: colour thermostabilizers, non-painting antioxidants and rubber and plastic lubricates. They also effectively decelerate prepolymerization of dienes on the stage of their rectification, and decrease combustibility of plasticized PVC.

Keywords: Non-polar olefin oligomers; functionalization; oxygen-; nitrogen-; silicon-containing compounds

RESULTS AND DISCUSSION

Macromolecular reactions are the modern way of synthesis of new high-molecular compounds, specially valuable in the cases, when such compounds could be hardly obtained or not obtained at all by different methods. The whole arsenal of synthetic organic chemistry may be used for obtaining various oligomer substances, based on relatively short list of accessible compounds, by the method of macromolecular reactions.

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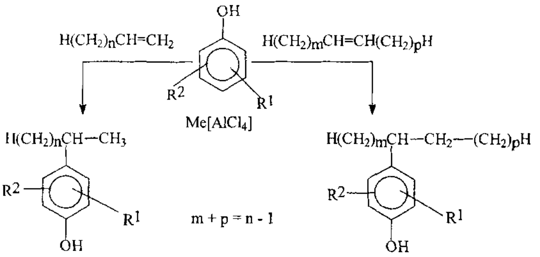
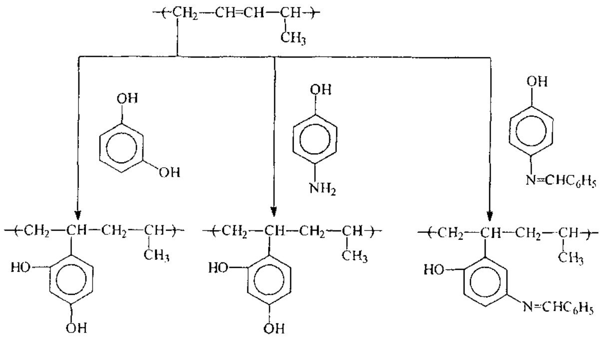
* Corresponding author.

Functionalization of non-polar oligomers of olefins and dienes by phenols and aminophenols with their further polymer-analogous transformations under soft experimental conditions was studied. Alkylation of phenols and aminophenols was conducted in the presence of electrophilic catalysts with decreased relative acidity comparing with $AlCl_3$ – complex salts of $Me[AlCl_4]$ type (Me = Li, Na, K) with the product output up to 98% (353 – 393 K, 2 – 6 hours). Expenditure of the reagents during synthesis was ozometrically controlled due to decrease of the non-saturation degree of initial oligomers. Either individual compounds with an end functional group or a mixture of oligomer products is formed in dependence on position and amount of $> C = C <$ bonds in accord with the amount and position (internal, end) of double bonds [1]:



$R^1 = R^2 = H$; $R^2 =$ o-, m-CH_3; $R^1 = H$, $R^2 =$ i-C_3H_7; $R^1 = R^2 =$ t-C_4H_9; $R^1 = H$, $R^2 =$ o-, m-, p-OH; $R^1 = H$, $R^2 =$ o-, p-N=CH-C_6H_5.

and (on the example of oligopyperylene chain):



Conditions of phenol and aminophenol alkylation by various oligomers are shown in Table I.

The data from Table I testify that complex salts of Me[$AlCl_4$] type are suitable and effective catalysts of selective alkylation of phenols by oligomers. They are highly active and selective in alkylation of phenols (in the reaction conducted according to classic mechanism of electrophilic substitution) under application of catalysts with relative acidity B ranged within 1–2 mg-eq./g cat. (B for $AlCl_3$ is 5.0 mg-eq./g cat.). Among the above mentioned sequence of catalysts sodium tetrachloraluminate (B = 1.6 mg-eq./g cat.) was chosen as mot effective and accessible one. In its presence functionalization of olefin and diene oligomers was made. Alkylation of phenols and aminophenols in the presence of Na[$AlCl_4$] is the accessible method of synthesis of oligomer phenols. The process proceeds easily and is not accompanied by side product formation. Interactions of benzylidenaminophenols with oligo–olefins proceeds under more rigid conditions, than for phenols (Tab. I). This is evidently connected with complication of electrophilic substitution as a consequence of electron density depletion in an aromatic nucleus, caused by the existence of electronacceptor benzylidenamino group.

Study of kinetics of phenol alkylation by oligo–olefins was conducted on the example of the model reaction of phenol with heptene-1 ($T = 343\,K$, $C_{phenol} = C_{olefin} = 2.4\,mol/l$; $C_{Na[AlCl_4]} = 0.24\,mol/l$). The process is guided by the rules of the second order reaction, the constant observed $K = (2.2 \pm 0.2) \cdot 10^{-5}\,l/mol \cdot s$ [2].

Thermostability of phenols alkylated by oligoisobutylenes with various $\overline{M}_n$ increases rapidly from 486 to 533 K for oligoisobutylenephenols with $\overline{M}_n$ up to 1200. Double increase of $\overline{M}_n$ increases temperature of the begining of thermal decomposition by 20° (Fig. 1). Evidently, the effect observed may be caused by OH group blockade in oligobutylenephenols by an alkyl chain obtaining bent conformation at large number of carbon atoms.

Suitable and relatively easy way of intraduction of phenol and aminophenol fragments into the composition of olefin and diene oligomers opens wide possibilities for their further polymer-analogous transformations. The reaction of oligomer phenols condensation with 3,4-dibrom-4-methyltetrahydropyrane in hexane. Some phenol esters were obtained with high output, which were quantitatively regroupped

TABLE I Alkylation of phenols and aminophenols by oligo–olefins

Phenol	*Catalyst*	*Reaction duration, hours*	*Product output, mass %*	[C = C], *mole (mole PIBP)*$^{-1}$	^{13}*C NMR spectrum, δ*, m.d.*	*Selectivity, rel. units*
			Oligoethylene ($\overline{M}_n$ = 1300)			
Phenol	$AlCl_3$	10	75	–	–	0.7
Phenol	$C_6H_5SO_3H$	4	46	–	–	0.4
Phenol	$Na[AlCl_4]$	2.5	96	0.012	135.5	0.9
2-Methylphenol	$Na[AlCl_4]$	2.5	96	0.015	135.2	0.9
3-Methylphenol	$Na[AlCl_4]$	3.0	93	0.021	134.8	0.9
4-Isopropylphenol**	$Na[AlCl_4]$	3.0	93	0.021	129.6	0.9
2, 6-Di-tert-butylphenol**	$Na[AlCl_4]$	4.0	89	0.033	125.2	0.9
o-Dioxybenzene	$Na[AlCl_4]$	2.5	93	0.021	149.0	0.9
m-Dioxybenzene	$Na[AlCl_4]$	2.5	96	0.012	122.8	0.9
n-Dioxybenzene	$Na[AlCl_4]$	2.5	90	0.030	131.6	0.9
2-Aminophenol***	$Na[AlCl_4]$	2.5	93	0.021	–	0.9
4-Aminophenol***	$Na[AlCl_4]$	2.5	98	0.006	–	0.9
2-Benzylidenamino-phenol***	$Na[AlCl_4]$	4.0	98	0.012	136.9	0.9
4-Benzylidenamino phenol***	$Na[AlCl_4]$	4.0	96	0.012	131.5	0.9
4-Isopropylphenol****	$Li[AlCl_4]$	2.5	91	0.023	–	0.9
m-Dioxybenzene	$Li[AlCl_4]$	2.0	95	0.015	–	0.9
4-Isopropylphenol**	$K[AlCl_4]$	2.5	93	0.021	–	0.9
m-Dioxybenzene	$K[AlCl_4]$	2.0	96	0.012	–	0.9
			Oligopropylene ($\overline{M}_n$ = 1400)			
Phenol	$C_6H_5SO_3H$	4.0	36	–	–	0.3
Phenol	$Na[AlCl_4]$	2.5	96	0.037	141.3	0.9
4-Isopropylphenol**	$Na[AlCl_4]$	3.0	94	0.056	135.3	0.9
m-Dioxybenzene	$Na[AlCl_4]$	2.5	98	0.019	128.5	1.0
4-Isopropylphenol**	$Li[AlCl_4]$	3.5	92	0.074	–	0.9
m-Dioxybenzene	$Li[AlCl_4]$	2.5	95	0.047	–	0.9
4-Isopropylphenol**	$K[AlCl_4]$	3.0	94	0.056	–	0.9
m-Dioxybenzene****	$K[AlCl_4]$	2.5	97	0.030	–	0.9
			Oligoisobutylene ($\overline{M}_n$ = 1100)			
Phenol	$C_6H_5SO_3H$	4.0	31	–	–	0.3
Phenol	$Na[AlCl_4]$	2.5	98	0.020	143.5	1.0
4-Isopropylphenol**	$Na[AlCl_4]$	3.0	96	0.040	137.5	0.9
m-Dioxybenzene	$Na[AlCl_4]$	2.5	98	0.020	130.7	1.0
4-Isopropylphenol**	$Li[AlCl_4]$	3.0	95	0.050	–	0.9
m-Dioxybenzene****	$Li[AlCl_4]$	2.0	96	0.048	–	0.9
4-Isopropylphenol**	$K[AlCl_4]$	3.0	96	0.040	–	0.9
m-Dioxybenzene****	$K[AlCl_4]$	2.0	94	0.060	–	0.9

Reaction conditions: T = 38 K, [Cat] = 0.5 mole (mole of oligo–olefin)$^{-1}$.

* Signal of carbon atom, bonded to oligomer radical;

** T = 393 K;

*** T = 373 K;

**** [Cat] = 0.10 mole (mole of oligo olefin)$^{-1}$, T = 393 K.

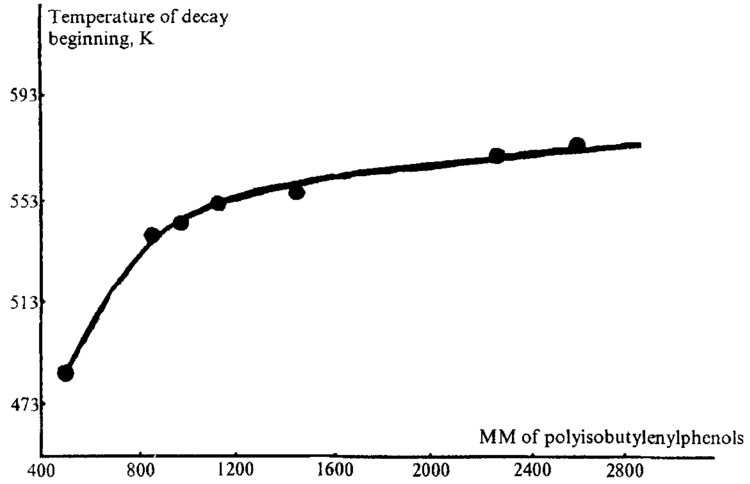
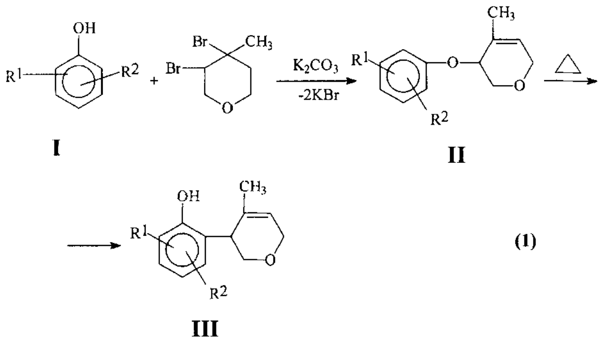


FIGURE 1 Dependence of temperature of thermal decomposition beginning for oligoisobutylenephenols on their molecular mass.

into pyranylphenols in *N*, *N*-diethylaniline medium according to Klauzen (Tab. II) [3]:



a) $R^1 = H, R^2 = 4-H-(-CH_2-CH_2-)_m-\underset{|}{C}H-CH_2-(-CH_2-CH_2-)_l-H,$

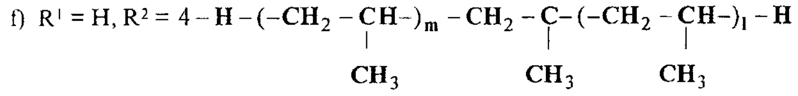
$m + l = n - 1$ (PE);

b) $R^1 = 2\text{-}CH_3$, $R^2 = 4\text{-PE}$;

c) $R^1 = 4\text{-}i\text{-}C_3H_7$, $R^2 = 2\text{-PE}$;

d) $R^1 = 2\text{-}N = CHC_6H_5$, $R^2 = 4\text{-PE}$;

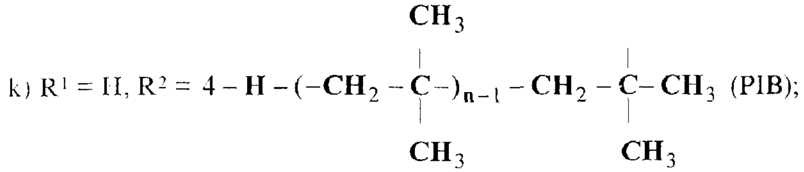
e) $R^1 = 4\text{-}N = CHC_6H_5$, $R^2 = 2\text{-PE}$;



f) $R^1 = H, R^2 = 4-H-(-CH_2-\underset{CH_3}{CH}-)_m-CH_2-\underset{CH_3}{C}-(-CH_2-\underset{CH_3}{CH}-)_l-H,$

m + l = n - l (PP);

g) R^1 = 2-CH_3, R^2 = 4-PP;
h) R^1 = 4-i-C_3H_7, R^2 = 2-PP;
i) R^1 = 2-N = CHC_6H_5, R^2 = 4-PP;
j) R^1 = 4-N = CHC_6H_5, R^2 = 2-PP;



k) $R^1 = H, R^2 = 4-H-(-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-)_{n-1}-CH_2-\overset{|}{\underset{CH_3}{C}}-CH_3$ (PIB);

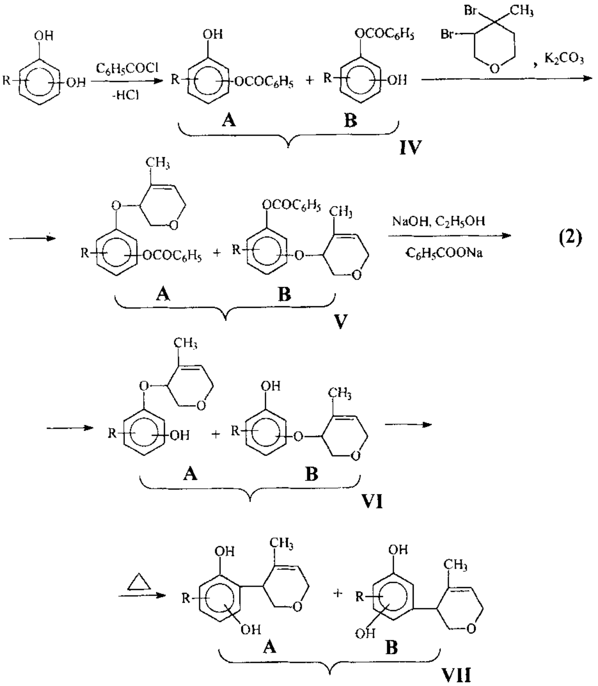
l) R^1 = 2-CH_3, R^2 = 4-PIB;
m) R^1 = 4-i-C_3H_7, R^2 = 2-PIB;
n) R^1 = 2-N = CHC_6H_5, R^2 = 4-PIB;
o) R^1 = 4-N = CHC_6H_5, R^2 = 2-PIB;

TABLE II Characteristics of oligomer one-atom phenols, benzylidenaminophenols and products of their regroupping

Index of	*Condensation (compounds II)*		*Regroupping (compounds III)*	
*compound**	*Product output,* %	δ_c**, *m.d.*	*OH-group content, mol/mol of oligo-olefinylphenol*	δ_c,** *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
k	96.1	148.6	0.98	144.8
l	96.0	148.3	0.95	144.6
m	91.8	143.9	0.96	138.8
n	90.9	149.9	0.98	145.8
o	90.1	153.5	0.94	140.7

* Indexes relate to the compounds with corresponding indexes from explanation to the reaction scheme (1);
** Signal for C atom, bonded to an oligomer fragment.

To introduce a pyranyl substituent into oligomer biatomic phenols only by a single HO-group, the second hydroxyl group must be protected [4]:

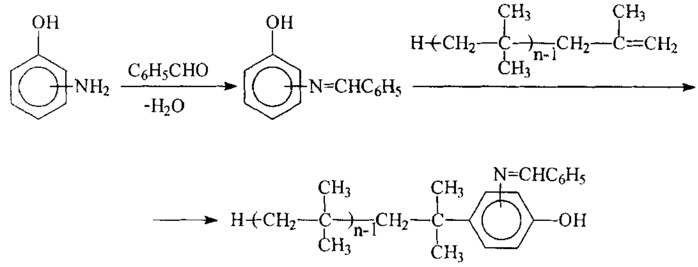


(2)

a) 2-OH, R = 4-PIB;
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 = 4-PP;
g) 2-OH, R = 4-PE;
h) 3-OH, R = 4-PE;
i) 4-OH, R = 2-PE.

Basing on ^{13}C NMR and gas-liquid chromatography the ratio of A and B isomers for oligomer 1,2-dioxybenzenes was found A : B = 1 : 1, and that for 1,3- and 1,4-dioxybenzenes-3 : 1. Introduction of a macroradical into an aromatic nucleus promotes more complete proceeding of the reaction and noticeable increase of the synthesis product yield comparing it with low-molecular analogs (Tab. III).

In the reaction with aminophenols for introducing an oligomer substituent into an aromatic nucleus aminophenols were preliminarily treated by a benzaldehyde:



Regroupping by Clausen was also studied on the sequence of aminophenols. There are practically no examples of implication of compounds containing pyranic cycle into the reaction. Condensation of aminophenols with 3, 4-dibrom-4-methyltetrahydro-pyrane and isomerization of the products may proceed by both HO- and H_2N- groups. In this case, that predetermines the direction of further regroupping:

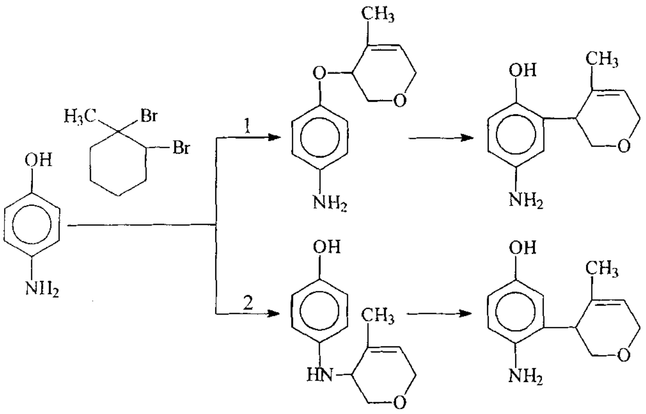


TABLE III Indexes of the compounds IV–VIII

*Letter index**	*Benzoylation (compounds IV)*			*Condensation (compounds V)*		*Hydrolysis (compounds VI)*			*Regroupping (compounds VII)****	
of compounds	*Yield, %*	*HO-group content, mol/mole of oligo–olefinphenol*	δ_c,**, *m.d.*	*Yield, %*	δ_c,** *m.d.*	*Yield, %*	*HO-group content, mol/mole of oligo–olefinphenol*	δ_c,** *m.d.*	*HO-group content, mol/mole of oligo–olefinphenol*	δ_c,** *m.d.*
a	98.5	2.80	144.9/150.2	89.0	149.8/149.5	99.1	1.40	150.2/139.5	2.80	146.2/133.2
b	99.0	2.80	135.9/137.2	91.0	142.2/142.6	95.3	1.40	130.9/135.8	2.80	132.0/132.9
c	98.4	2.80	139.4/145.9	88.2	145.8/145.3	98.3	1.40	150.1/139.4	2.80	147.2/137.3
d	98.0	2.30	142.7/143.6	88.1	144.7/143.9	96.1	1.15	147.4/137.3	2.30	138.7/135.1
e	99.0	2.16	133.7/135.4	90.1	140.0/140.2	98.4	1.08	135.0/133.7	2.16	130.2/129.7
f	98.5	2.18	137.3/142.7	89.3	143.6/144.1	99.0	1.09	142.0/137.4	2.18	138.8/135.1
g	98.8	0.58	137.0/142.0	90.2	142.1/141.9	98.2	0.29	141.8/137.1	0.58	133.0/130.6
h	98.4	0.56	128.0/129.5	91.8	134.3/134.6	99.5	0.28	129.3/128.1	0.56	124.3/125.0
i	98.4	0.56	131.1/138.0	91.9	137.9/137.6	97.9	0.28	138.2/131.7	0.56	133.3/129.4

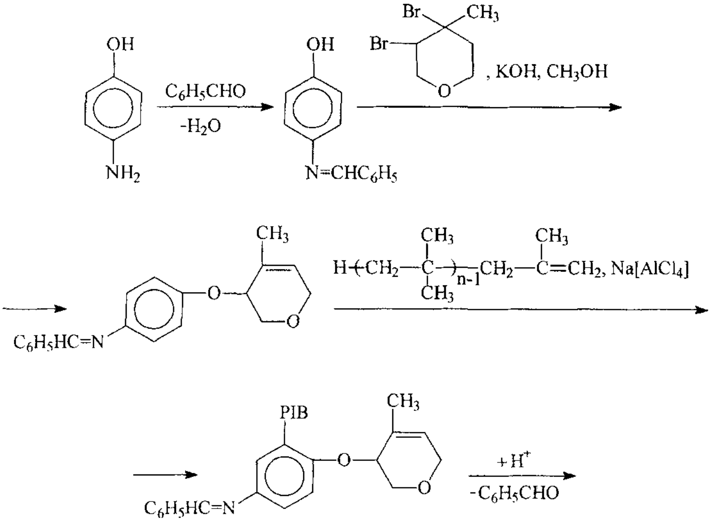
* Letter indexes relate to compounds, obtained by the reactions (2);

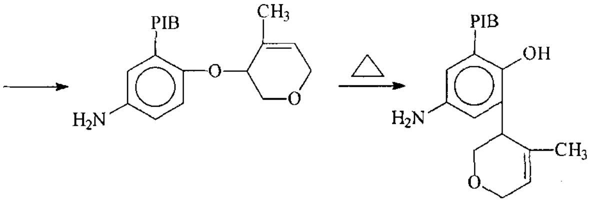
** Numerator marks the value for the isomer A, and denominator – for the isomer B;

*** Quantitative yield.

The conditions of directed synthesis were determined for one of phenolic groups only. Regroupping was primarily studied on low-molecular analogs for further application of it to high-molecular objects. To conduct the process by OH-group it is necessary to apply such strong bases as KOH in methanol (Direction 1). As a result of reaction a product of condensation by amino group accompanies that by hydroxyl. Separation and excretion of the products is made by the colon chromatography technique. It was found experimentally that the ratio of O- and N-products is 2:1, and the direct product yield falls with 40 – 50% depending on the composition of the initial aminophenol.

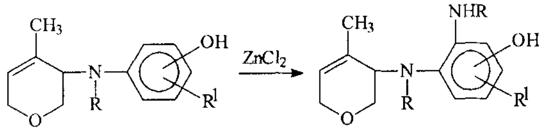
To study the regroupping by Clausen in the sequence of high-molecular aminophenols in order to aim the process of electrophilic substitution into the aromatic nucleus at alkylation the amino group was preliminarily transfered into an asometynic one. The protection was removed just before the regroupping. The regroupping of high-molecular products by Clausen was performed under the conditions selected on low-molecular analogs, *i.e.*, thermally in the *N*, *N*-diethylamine medium (4 – 5 hours, 443 K). Migration of a pyranilic radical happens only into the ortho-position of benzolic circle as the most probable variant because of the absence od substituents.





Contrary to the condensation of aminophenols by HO-group, the direction 2 is realized at the interaction of ingradients in the medium of a base with higher basicity, than the aminophenol (triethylamine) possesses. While phenylic esters are characterized by thermal regrouping by Clausen, [*N*-(4-methyl-5, 6-dihydro-2H-pyranyl-5)amino]-phenols are isomerized only in the presence of catalytic properties of Louis acids, $ZnCl_2$, for example (Tab. IV).

To obtain phosphorous-containing compounds, composing a separate group of antipyrenes of oligomer nature, the interaction of



R = H, C_6H_5; R^1 = PIB

high-molecular phenols and aminophenols with triphenylphosphite was sutdied. In this case polymer-analogous transformations present re-etherification of phosphite by an oligomer phenol, that proceeds under soft conditions, wihtout a catalyst and practically with a quantitative yield (Tab. V). A monophosphite is formed at equimolar ratio of initial oligomers and trimethylphosphite. In dependence on the oligomer phenol:triphenylphospite ratio (1:1 or 1:2) mono- or disubstituted phosphites were separated. As a consequence of ortorientation of hydroxyl groups at etherification of oligomer 1, 2-dioxybenzene the obtaining of a cyclic phosphite was observed. As in the case of low-molecular 4-oxydiphenylamine at the interaction with thriphenylphosphite a substitution of three phenoxylic radicals, the oligomer 4-oxydiphenylamine evidently substituted only phenoxyl radical in the $P(OC_6H_5)_3$ molecule due to steric hindrences.

TABLE IV Synthesis of low-molecular and oligomer pyranylaminophenols and their oxy- and amino-regroupping by Clausen

Compound	R_f	*Yield,* %	*Found/Calculated, %* *C*	*H*	*N*	^{13}*C NMR spectrum,* δ*, *m.d.*
4-(4-methyl-5,6,-dihydro-2H-pyranyl-5-oxy) aminobenzene	0.57	48	70.49/70.24	7.55/7.32	7.01/6.82	151.1
2-(4-methyl-5,6-dihydro-2H-pyranyl-5-6-dihydro-2H-pyranyl-5-oxy) aminobenzene	0.33	40	70.07/70.24	7.21/7.32	6.73/6.82	150.5
1-(4-methyl-5,6-dihydro-2H-pyranyl-5-oxy)-4-(*N*-aminophenyl)benzene	0.59	50	77.00/76.86	6.92/6.76	5.13/4.98	153.7
2-(4-methyl-5,6-dihydro-2H-pyranyl-5-oxy)-4-aminophenol	0.28	83	70.61/70.24	7.50/7.32	6.99/6.82	148.9
2-(4-methyl-5,6-diyhydro-2H-pyranyl-5-oxy)-6-aminophenol	0.33	69	70.57/70.24	7.48/7.32	6.60/6.82	150.8
2-(4-methyl-5,6-dihydro-2H-pyranyl-5)-5-(*N*-phenyl)aminophenol	0.15	64	76.58/76.86	6.79/6.76	4.63/4.98	150.8
4-(4-methyl-5,6-dihydro-2H-pyranyl-5-oxy)-benzylidenaminobenzene	0.63	68	77.54/77.81	6.70/648	4.96/4.77	149.2
2-(4-methyl-5,6-dihydro-2H-pyranyl-5-oxy)-benzylidenaminobenzene	0.29	62	77.96/77.81	6.33/6.48	4.98/4.77	148.5
5-(4-methyl-5,6-dihydro-2H-pyranyl-5-oxy)-5-oligoisobutylene-benzylidenaminobenzene	–	81	83.61/83.83	12.37/12.28	1.21/1.18	150.9

1-(4-methyl-5,6-dihydro-2H-pyrnayl-5-oxy)-3-oligoisobutylenebenzylidenaminobenzene	–	89	83.99/83.83	12.12/12.28	1.35/1.18	149.3
4-(4-methyl-5,6-dihydro-2H-pyranyl-5-oxy)-5-oligoisobutylenylamino benzene	–	99	82.74/82.90	12.60/12.81	1.45/1.27	152.0
2-(4-methyl-5,6-dihydro 2H-pyranyl-5-oxy)-5-oligoisobutylenylaminophenol	–	98	83.15/82.90	12.98/12.81	1.41/1.27	151.3
2-(4-methyl-5,6-dihydro-2H-pyranyl-5)-4-amino-6-oligoisobutylenylphenol	–	95	82.65/82.90	12.60/12.81	1.03/1.27	149.0
2-(4-methyl-5,6-dihydro-2H-pyranyl-5-oxy)-6-amino-4-oligoisobutylenylphenol	–	93	83.27/83.90	13.01/12.81	1.40/1.27	150.1
1-(4-methyl-5,6-dihydro-2H-pyranyl-5-oxy)-5-[*N*-amino(4-oligoisobutylenylphenyl)]benzene	–	91	83.88/83.67	12.29/12.41	1.40/1.19	154.0
2-(4-methyl-5,6-dihydro-2H-pyranyl-5-oxy)-5-[*N*-(4-oligoisobutylenyl)-phenyl]aminophenol	–	92	83.30/83.67	12.57/12.41	1.36/1.19	151.4

TABLE IV (Continued)

Compound	R_f	*Yield,* %	*Found/Calculated,* %			^{13}C *NMR spectrum,* δ*, *m.d.*
			C	*H*	*N*	
2-[*N*-(4-methyl-5,6-dihydro-2H-pyranyl-5)-amino]phenol	0.54	86	70.58/70.24	7.54/7.32	7.13/6.82	139.7
4-[*N*-(4-methyl-5,6-dihydro-2H-pyranyl-5)-amino]phenol	0.38	83	70.69/70.24	7.49/7.32	6.99/6.82	144.2
4-[*N*-phenyl-(4-methyl-5,6-dihydro-2H-pyranyl-5)-amino]phenol	0.50	81	77.01/76.86	6.95/6.76	5.13/4.98	144.8
4-oligoisobutylenyl-2-[*N*-(4-methyl-5,6-dihydro-2H-pyranyl-5)amino]phenol	–	95	83.09/82.60	13.34/12.95	1.57/1.26	137.4
2-oligoisobutylenyl-2-[*N*-(4-methyl-5,6-dihydro-2H-pyranyl-5)amino]phenol	–	93	83.01/82.60	13.28/12.95	1.49/1.26	141.5
3-(4-methyl-5,6-dihydro-2H-pyranyl-5)-2-aminophenol	0.48	85	79.03/70.24	7.46/7.32	7.04/6.82	143.0
3-(4-methyl-5,6-dihydro-2H-pyranyl-5)-4-aminophenol	0.30	81	70.62/70.24	7.21/7.32	7.13/6.82	146.4
3-(4-methyl-5,6-dihydro-2H-pyranyl-5)-4-(*N*-phenyl)aminophenol	0.28	84	77.15/76.86	6.89/6.76	5.20/4.98	147.1

4-oligoisobutylenyl-3-(-4-methyl-5,6-dihydro-2H-pyranyl-5)-2-aminophenol	–	98	82.37/82.60	13.34/12.95	169.1.26	140.5
4-oligoisobutylenyl-5-(4-methyl-5,6-dihydro-2H-pyranyl-5)-4-aminophenol	–	96	82.20/82.60	13.23/12.95	1.01/1.26	143.3
4-oligoisobutylenyl-5-(4-methyl-5,6-dihydro-2H-pyranyl-5)-4-(*N*-phenyl)-aminophenol	–	90	83.51/83.38	12.32/12.45	1.56/1.18	143.9

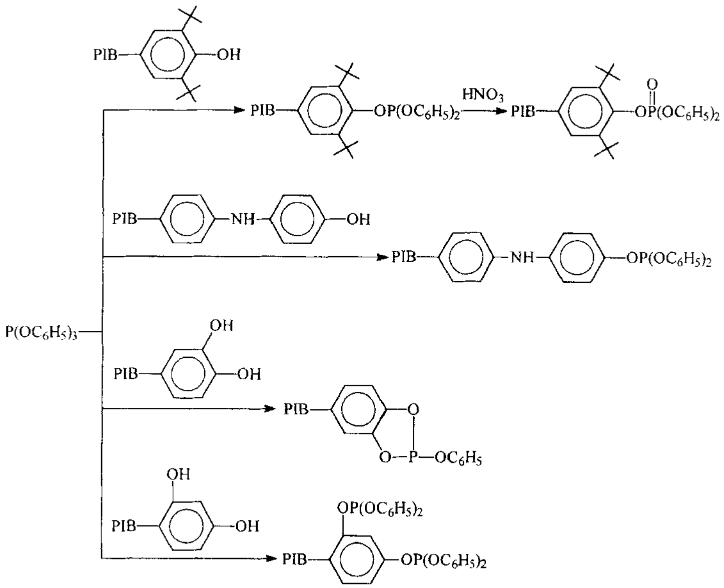
* Signal from C atom of aromatic cycle, bound to oxygen atom.

TABLE V Phosphorylation of oligomeric phenols and aminophenols

No.	*Oligomeric compounds*	*Reaction duration, hour*	*Reaction temperature, K*	*Residual pressure, mm Hg*	*Phenol: TPP* ratio, mole*	*MM of phosphorylated product*	*Found, %:P/ Calculated, % : P*	*^{31}P NMR spectrum, δ_P, m.d.*
1	(2,6-di-tert-butyl-4-oligoisobutylenyl)diphenylphosphite	3.0	383	10	1:1	1521	1.68/17.3	122.5
2	2-oligoisobutylenyl-phenylene-1,4-bis(diphenylphospite)	2.5	373	10	1:2	1652	3.30/3.41	120.9
3	4-oligobutylenyl-phenylene-1,3-bis(diphenylphosphite)	2.5	373	10	1:2	1652	3.31/3.11	120.5
4	(3-oligoisobutylenyl-phenylene-1,2)phenylphosphite	2.5	373	10	1:1	1337	2.02/2.17	140.1
5	[4-(*N*-oligoisobutylenylamino)-phenyl]diphenylphosphite	2.0	363	8	1:1	1400	2.00/2.10	121.1
6	[2-(*N*-oligoisobutylenylamino)-phenyl]diphenylphosphite	2.5	383	8	1:1	1400	1.85/2.10	122.3
7	4-[*N*-(4-oligoisobutylenylphenyl)-amino]phenyl-diphenylphosphite	2.0	383	10	1:1	1506	1.89/1.98	122.0
8	(2,6-di-tert-butyl-4-oligopropylenyl)diphenylphosphite	3.0	383	10	1:1	1821	1.35/1.48	122.4
9	2-oligopropylenylphenylene-1,4-bis(diphenyl)phosphite	2.5	373	10	1:2	1952	2.74/2.83	120.8
10	(4-oligopropylenylphenylene-1,3-bis)diphenylphosphite	2.5	373	10	1:2	1952	2.69/2.83	120.4
11	(3-oligopropylenylphenylene-1,2)-phenylphosphite	2.5	363	8	1:1	1637	1.57/1.70	140.0
12	[4-(*N*-oligopropylenylamino)-phenyl]diphenylphosphite	2.0	373	10	1:1	1730	1.66/1.74	121.0
13	[2-(*N*-oligopropylenylamino)-phenyl]diphenylphosphite	2.5	363	8	1:1	1730	1.61/1.74	122.2
14	4-[N-(4-oligopropylenylphenyl)-amino]phenyl-diphenylphosphite	2.0	373	10	1:1	1806	1.43/1.53	122.0

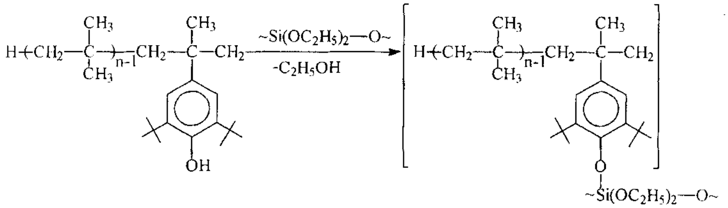
15	(2,6-di-tert-butyl-4-oligoethylenyl)-diphenylphosphite	2.5	383	10	1:1	1721	0.41/0.43	122.3
16	2-oligoethylenylphenylene-1,3-bis(diphenylphosphite)	2.0	363	8	1:2	1852	1.50/1.63	120.7
17	4-oligoethylenylphenylene-1,3-bis(diphenylphosphite)	2.0	363	8	1:2	1852	1.50/1.63	120.2
18	(3-oligoethylenylphenylene-1,2)-phenylphosphite	2.0	363	8	1:1	1537	1.00/1.05	140.0
19	[4-(*N*-oligoethylenylamino)phenyl]-diphenylphosphite	1.5	353	6	1:1	1630	0.49/0.54	121.0
20	[2-(*N*-oligoethylenyl)aminophenyl]-diphenylphosphite	2.0	353	6	1:1	1630	0.44/0.54	122.3
21	4-[*N*-(4-oligoethylenylphenyl)-aminophenyl]diphenylphosphite	1.5	353	6	1:1	1706	0.42/0.51	122.0
22	(2,6-di-tert-butyl-4-oligopyperilenyl)diphenylphosphite	3.5	383	10	1:1	3943	4.79/4.84	122.2
23	2-oligopyperilenylphenylene-1,4-bis(diphenylphosphite)	3.0	373	10	1:2	5059	8.08/8.23	120.8
24	4-oligopyperilenylphenylene-1,3-bis(diphenylphosphite)	3.0	373	10	1:2	5059	8.10/8.23	120.3
25	(3-oligopyperilenylphenylene-1,2)-phenylphosphite	3.0	373	10	1:1	2962	7.03/7.11	140.1
26	[2-(*N*-oligopyperilenylamino)-phenyl]diphenylphosphite	3.0	363	8	1:1	3515	5.60/5.78	122.5
27	4-[*N*-(4-oligopyperilenylphenyl)-amino]phenyl-diphenylphosphite	3.0	363	8	1:1	3786	4.82/4.91	122.1

* TTP is triphenylphosphite.



High yield of corresponding phosphates was obtained by further oxidation of oligomer phosphites under soft conditions.

To broaden the frames of application of oligomers with phenolic and aminophenolic fragments their functionalization by ethylsilicates was conducted, by ES-40 brand oligomer ethylsilicate ($n = 5$), in particular. Reaction of oligomer phenols with ethylsilicate proceeds without a catalyst at 433–443 K up to complete excretion of calculated volume of ethanol. The number of ethyl groups re-etherified per a fragment of oligomer phenol was varied by the ratio of initial compounds.



Products of functionalization of olefin and diene oligomers by oxygen-, nitrogen-, and phosphorus-containing compounds are the effective complex stabilizers of chlorine-containing polymers. For example, high-molecular antioxidants decrease the rate of dehydrochlorination of chlorinated ethylenepropylic rubber (CSREP) much stronger than their low-molecular analogs. Differences in their efficiency are most well observed in the oxidative medium (Fig. 2). Oligoisobutylenylphenols decrease the rate of HCl elimination by 2.5 times (down to the values, observed in the inert medium), and low molecular phenols – by 1.5 times only.

The study of kinetics of CSREP dehydrochlorination in the presence of high-molecular antioxidants with various molecular masses has shown that the efficiency of the stabilizing effect does not depend on the length of oligomer radical (Tab. VI).

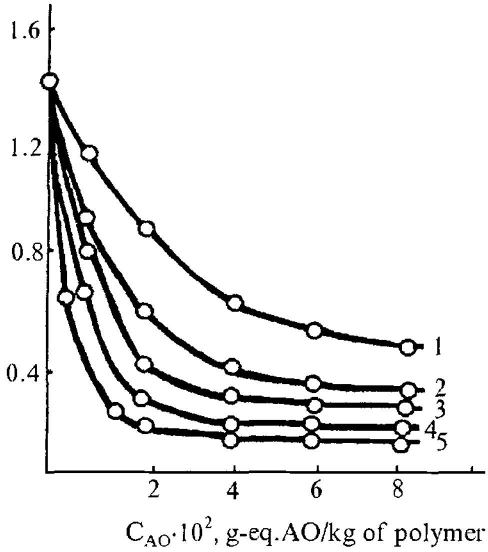


FIGURE 2 Dependency of CSREP dehydrochlorination rate on the concentration of phenolic antioxidants.

(1) 1,2-dioxybenzene;
(2) 2,6-di-tert-butyl-4-methylphenol
(3) 4-oligoisobutylenyl-1,2-dioxybenzene;
(4) 3-oligopyperilenyl-1,4-dioxybenzene;
(5) 4-oligopyperilenyl-1,2-dioxybenzene.

TABLE VI Depedency of the rate of HCl elimination from CSREP on AO structure ($C_{AO} = 1.9 \cdot 10^{-2}$ g-eq. AO/kg of polymer)

AO	*Polymerization degree in oligo-isobutylenyl*	$V_{HCl} \cdot 10^7$, *mol HCl/(mol Cl in CSREP)·s* *in air*	*in nitrogen*
4-oligoisobutylenyl-1,2-dioxybenzene	12	3.10	2.00
	14	3.06	2.04
	20	3.40	2.00
	27	3.11	1.98
	63	3.10	2.02
4-oligoisobutylenyl-1,3-dioxybenzene	12	3.21	2.05
	20	3.16	2.10
	63	3.25	3.13
4-oligoisobutylenyl-1,4-dioxybenzene	12	3.93	2.10
	14	3.26	2.12
	20	3.31	2.10
	27	3.25	2.10
	63	3.30	2.15
1,2-dioxybenzene	–	5.30	2.33
1,4-dioxybenzene	–	5.00	2.50
In the absence of AO	–	7.50	3.30

Dependence of PVC dehydrochlorination rate on the concentration of studied antioxidants is different from the corresponding dependence for CSREP (Fig. 3). Introduction of two-atom phenols decreases the rate of HCl elimination from PVC. However, growth of their concentration over $1 \cdot 10^{-3}$ g-eq. OH/kg PVC induces a growth of polymer dehydrochlorination rate, *i.e.*, two-atom phenols display critical concentration, characteristic for phenols, the overwhelming of which leads to an increase of PVC decomposition rate [5].

Oligobutylenyl-alkylated two-atom phenols significantly improve the processing of PVC, increasing the melt index of the polymer (J_p) that is 0.24 g/10 min. for rigid PVC-compositon in the absence of synthesized compounds (Fig. 4).

The dependence of CSREP dehydrochlorination rate on the content of phenols and aminophenols, alkylated by oligopyperilene, comparing with their low-molecular analogs, including industrial antioxidant agidol-1, is shown in Figure 5.

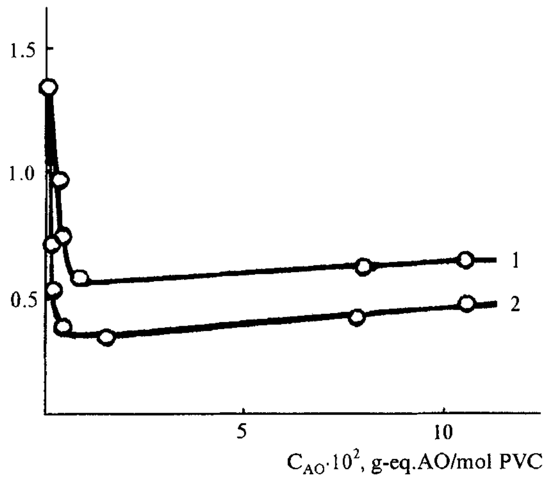


FIGURE 3 Dependency of PVC dehydrochlorination rate on the concentration of phenolic antioxidants.

(1) 1, 2-dioxybenzene;
(2) 4-oligoisobutylenyl-1, 2-dioxybenzene.

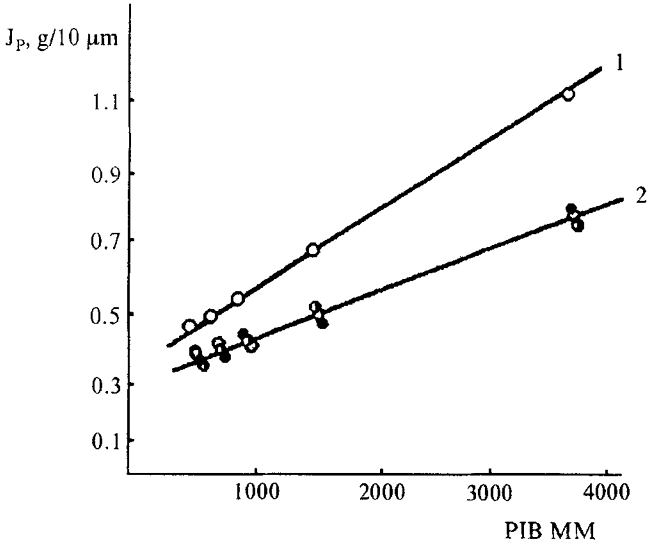


FIGURE 4 Dependency of the fluidity index of rigid PVC composition melt on the molecular mass of PIB (2 mass parts per 100 mass parts of PVC).

(1) 2, 6-di-tertbutyl-4-oligoisobutylenylphenol (O), 4-oligoisobutylenyl-1, 2-dioxybenzene (•), 3-oligoisobutylenyl-1, 4-dioxybenzene (Ø);
(2) 2-(4-methyl-5, 6-dihydro-2H-pyranyl)-4-oligoisobutylenylphenol.

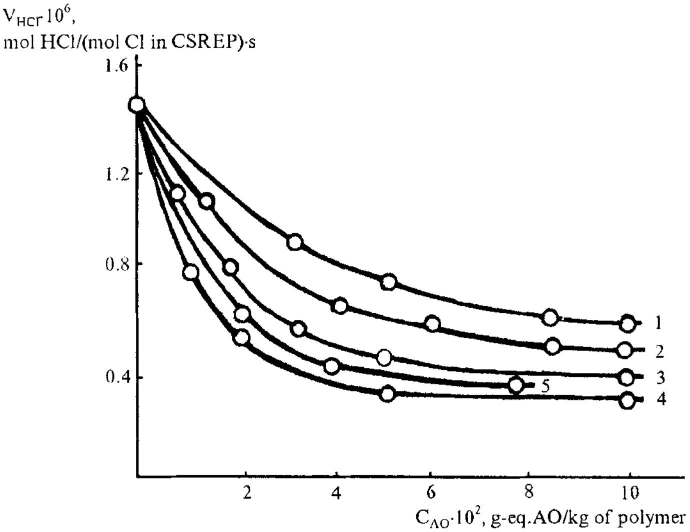


FIGURE 5 Dependency of CSREP dehydrochlorination rate on the concentration of aminophenolic antioxidans.

(1) 4-benzylidenamino-2-oligopyperilenylphenol;
(2) 4-benzylidenaminophenol;
(3) 4-oligopyperilenylaminophenol;
(4) 4-aminophenol;
(5) 2, 6-di-tertbutyl-4-methylphenol.

CSREP samples stabilized by functionalized oligopyperilenes, kept color and elasticity during 10 – 12 hours of degradation, whereas in the presence of low-molecular antioxidants (in the same cases) inadmissible change of coloring was observed, accompanied by cracking of films already after 3.5 ± 0.5 hours at 423 K. Oligopyperilenylaminophenols displayed no such a significant difference in effectiveness of stabilizing effect comparing with their low-molecular analogs. However, a significant decrease of dehydrochlorination rate of chlorine-containing polymers was observed at their combined introduction comparing with the effect of individual compounds (Fig. 6). No synergism was observed for low-molecular compounds (Tab. VII).

The compounds synthesized possess properties of polyfunctional chemicals-additives for some chlorine-containing polymers (chlori-

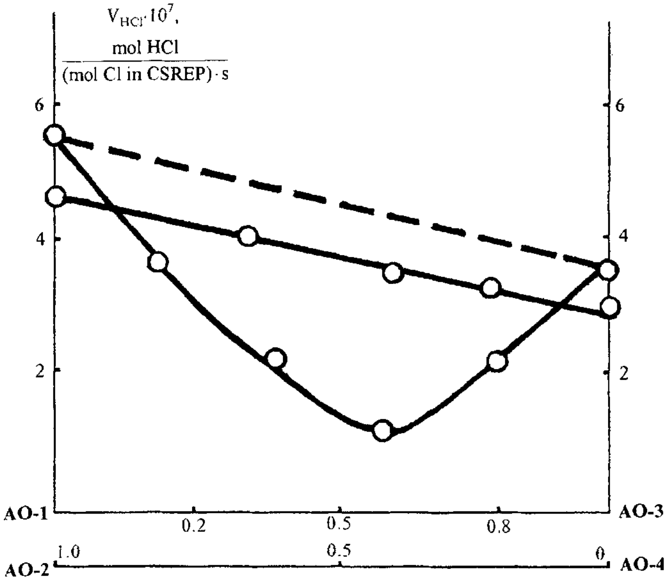


FIGURE 6 Dependency of CSREP dehydrochlorination rate on the ratio of individual components in the mixture of aminophenolic antioxidants.

(1) Mixture of 4-benzylidenamino-2-oligopyperilenylphenol with 4-oligopyperilenylaminophenol;
(2) Mixture of 4-benzylidenaminophenol with 4-aminophenol; (Total concentration of antioxidant is $6\cdot10^{-2}$mol AO/kg polymer).

TABLE VII Reaction rates of thermo-oxidative dehydrochlorination of haloid-containing polymers in the presence of high-molecular antioxidants (423 K, in air)

Antioxidant ($C = 6\cdot10^{-2}$ *mole of AO/kg of polymer*)	*Process rate,* $V_{HCl}\cdot10^6$, *mole of HCl/(mole of Cl)·s*	
	CPE	*CSREP*
2-oligopyperilenyl-1,4-dioxybenzene	0.15	0.25
4-oligopyperilenyl-1,2-dioxybenzene	0.12	0.20
4-oligopyperilenylaminophenol	0.19	0.33
4-benzylidenamino-2-oligopyperilenylphenol	0.38	0.65
4-benzylidenaminophenol	0.28	0.48
1,2-dioxybenzene	0.34	0.58
4-aminophenol	0.19	0.32
4-methyl-2,6-di-tertbutylphenol	0.21	0.36
Synergic mixture of AO	0.08	0.12
Without AO	0.83	1.42

nated ethylene-propylic rubber, CEPR; triple chlorinated ethylene-proplic rubber, TCEPR; chlorosulfopolyethylene-CSPE; chloropolyethylene – CPE, polyvinylchloride – PVC).

The inhibiting effect of synthesized oligomer phosphites were estimated:

a) by effectiveness of inhibition of radical prepolymerization of diene monomers (Tab. X);
b) by inductive oxidation period (τ) of polyisoprene rubber, determined by chemiluminescence technique (CL) by beginning of intensive lightening of stabilized rubber samples (Fig. 7);
c) by the 'plasticity preservation index' (PPI) of the samples of isoprene rubber and butadiene co-polymer with α-methylstyrene (Tab. XI).

The data from Tables X and XI testify that phosphites based on oligomer phenols and aminophenols effectively decelerate prepolymerization of diene on the stage of their rectification, decrease combustibility of pastisized PVC and protect rubbers from thermooxidative degradation providing preservation of necessary plastoelastic properties together with the high induction period.

The study of therooxidative stability of polypropylene and industrial oil by the induction period of oxygen absorption in the presence of low-molecular, as well as oligomer pyranylphenols, showed that they are rather effective stabilizers – antioxidants (Tab. XII). Introduction of an oligomer radical into a pyranylphenol molecule does not practically affect its efficiency, and at therooxidation of polypropylene it significantly increase the inhibiting effect in thermooxidative decay of industrial oils. This is apparently connected with better solubility of an oligomer antioxidant in oil comparing with the corresponding low-molecular analog. At the application of an oligomer antioxidant in polypropylene its better compatibillity is evidently compensated by lower mobility in the polymer matrix. In this case, consequently, efficiencies of low- and high-molecular analogs are virtually the same.

Application of oligomer [*N*-(4-methyl-5, 6-dihydro-2H-pyranyl-5)amino]phenols is most valuable for prevention of labricant oxidation, because introduction of an oligomer radical increases its protective properties, simultaneously decreasing its volatility. More-

TABLE VIII The effect of synthesized compounds on thermo- and color stability of chlorine-containing polymers (448 K, air, C_{AO} = 1 mass part)*

Compound	*PVC*		*CPE*		*CSPE*		*TCSPE*	
	τ, min	*color, points*	*τ, min*	*color, points*	*τ, min*	*color, points*	*τ, min*	*color, points*
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-isopropyl-2-oligopropylenylphenol	–	–	33	3.0	–	–	29	3.0
phenol alkylated by SPE	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 TSPE	45	3.0	39	3.0	35	3.0	34	3.5
4-isopropyl-2-oligopyperilenylphenol	54	3.0	50	2.5	46	2.0	37	2.5
1,3-dioxybenzene alkylated by SPE	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-dioxybenzene alkylated by TSPE	56	2.0	50	2.0	48	1.5	37	2.0
2-oligopyperilenyl-1,4-dioxybenzene	65	2.5	60	2.5	55	2.0	44	2.5
2-oligoethylenylaminophenol	–	–	–	–	4–	3.5	–	–
4-oligopropylenylphenol	–	–	42	3.5	–	–	37	3.5
2-aminophenol alkylated by SPE	–	–	–	–	42	3.5	39	3.5
4-oligopyperilenylaminophenol	–	–	56	3.5	50	3.5	41	4.0
2-benzylidenaminophenol alkylated by SPE	33	3.5	30	3.0	28	2.5	–	–
2-benzylidenamino-4-oligoisobutylenylphenol	40	3.0	35	3.0	28	2.5	–	–
4-benzylidenaminophenol alkylated by TSPE	–	–	40	3.0	–	–	29	3.0
4-benzylidenamino-2-oligopyperilenylphenol	52	3.0	48	2.5	45	3.0	35	3.0
Synergic mixture of 4-benzylidenamino-2-oligopyperilenylphenol with 4-oligopyperilenylaminophenol	–	–	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 marks thermostability duration (τ, min); denominator marks color stability (points by 'Synmero' scale).

TABLE IX The effect of oligomeric pyranylphenols on thermo- and color stability of haloid-containing polymers (448 K, air, C_O = 1 mass part)*

Compound	*PVC*		*CPE*		*CSREP*		*CSPE*	
	τ, min	*color, points*	*τ, min*	*color, points*	*τ, min*	*color, points*	*τ, min*	*color, points*
2-(4-methyl-5, 6-dihydro-2H-pyranyl)-4-oligoisobutylenylphenol	54	1.5	58	1.5	–	–	47	1.5
2-(4-methyl-5,6-dihydro-2H-pyranyl)-4-oligopropylenylphenol	51	1.5	44	1.5	–	–	34	2.5
2-(4-methyl-5,6-dihydro-2H-pyranyl)-4-oligoethylenylphenol	48	2.0	49	1.0	–	–	38	2.0
3-(4-methyl-5,6-dihydro-2H-pyranyl)-4-oligoisobutylenyl-1, 2-dioxybenzene	79	1.5	61	1.5	–	–	51	1.5
3-(4-methyl-5,6-dihydro-2H-pyranyl)-4-oligopropylenyl-1, 2-dioxybenzene	75	1.5	59	1.5	–	–	49	1.5
3-(4-methyl-5,6-dihydro-2H-pyranyl)-4-oligoethylenyl-1, 2-dioxybenzene	69	1.5	51	–	–	42	2.0	
2-(4-methyl-5,6-dihydro-2H-pyranyl)-4-oligoisobutylenyl-6-benzyliden-aminophenol	43	2.0	–	–	33	2.5	29	2.5
2-(4-methyl-5,6-dihydro-2H-pyranyl)-4-oligopropylenyl-6-benzylidenaminophenol	41	2.0	–	–	31	2.5	27	2.5
2-(4-methyl-5,6-dihydro-2H-pyranyl)-4-oligoethylenyl-6-benzylidenaminophenol	39	2.0	–	–	28	2.5	25	3.0
2,6-di-tertbutyl-4-methylphenol	20	4.5	24	4.5	20	4.5	17	3.0

over, oligomer [*N*-(4-methyl-5, 6-dihydro-2H-pyranyl-5)amino]phenols increase viscosity of oils, *i.e.*, may be antioxidative and thickening additives, simultaneously.

Introduction of a volumeric macroradical of oligomer phenol into ethylsilicate significantly improves its hydrophobic properties. For

TABLE X Comparative inhibiting activity of oligomer phosphorylated phenols and aminophenols in thermopolymerization of dienes

Monomer	*Inhibitor**	*Inhibitor concentration, mass %*	*Inhibition conditions*		*Inhibition effect*
			τ, hour	*T, K*	E_{in}, *relat.%*
Divinyl	2	0.005	24	343	99.4
		0.030	24	343	99.5
		1.000	24	343	99.5
	13	0.030	36	34	99.9
		0.030	48	343	99.5
		0.030	72	343	99.5
Isoprene	10	0.005	24	353	99.3
		0.030	24	353	99.5
		1.000	24	353	99.7
	22	0.030	36	343	99.5
		0.030	48	343	99.4
		0.030	72	343	99.4
Pyperilene	5	0.005	24	353	99.3
		0.030	24	353	99.5
		1.000	24	353	99.7
	28	0.030	36	353	99.6
		0.030	48	353	99.4
		0.030	72	353	99.4
Divinyl	tris(4-phenylamino-phenyl)-phosphite	0.030	24	353	99.2
Isoprene		0.030	24	353	99.0
pyperilene		0.030	24	353	98.9
Divinyl	4010 NA	0.030	24	343	96.5
Isoprene		0.030	24	353	97.1
Pyperilene		0.030	24	353	96.8

* The inhibitor number corresponds to the number of compound in Table V.

example impregnation of soft wood samples (linden, birch, poplar, *etc.*) by functionalized ethylsilicates decreases water absorption by more than 11 times, and demonstrates good adhesion to the surface tested.

CONCLUSION

The functionalization of non-polar oligomer of olefins and dienes by phenols and aminophenols with further polymer-analogous transformation of obtained compounds was performed under soft experimental conditions. The substances synthesized are chemicals-additives of polyfunctional action: color- and thermostabilizers, non-coloring

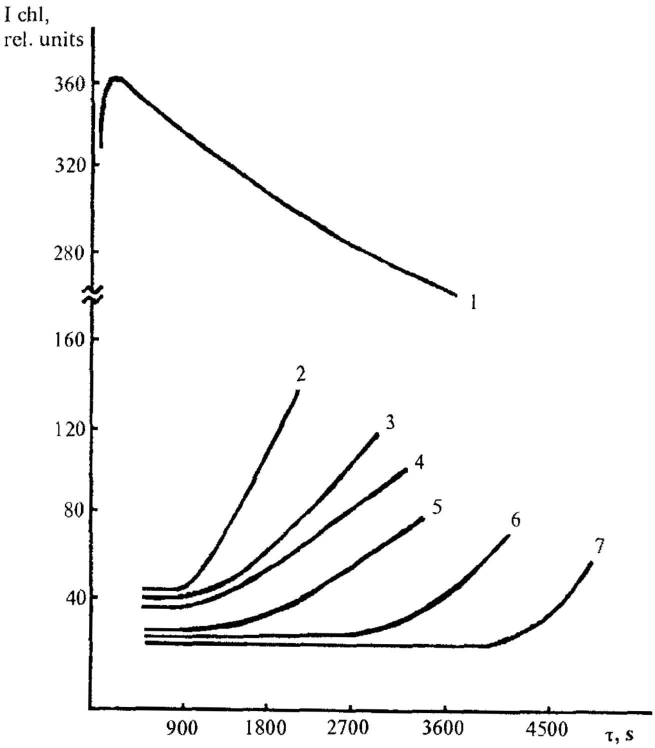


FIGURE 7 Dependency of chemiluminescence lightening intensity on the time of oxidation by SCI-3 (403 K, oxygen, $C_{in} = 3.4 \cdot 10^{-4}$ mol/mol).

(1) 7-In the absence of inhibitor;
(2–7) In the presence of inhibitor;
(3) 4-oligopyperilenyl-phenylene-1, 3-bis(diphenylphosphite);
(4) 2-oligopyperilenyl-phenylene-1, 4-bis(diphenylphosphite);
(5) tris(4-phenylaminophenyl)phosphite;
(6) [4-(*N*-oligopyperilenylamino)phenyl]diphenylphosphite;
(7) 4-[*N*-(4-oligoperilenylphenyl)amino]phenyl-diphenylphosphite.

antioxidants and lubricants of rubbers and plastics; effective decelerate prepolymerization of dienes on the stage of their rectification and decrease combustibility of plasticized PVC; may be used as antioxidative, thickening additives to oils, and hydrophobing agents of double action for water-sensitive materials, soft woods, for example.

TABLE XI Characteristics of effectiveness of oligomer phosphites at oxidation by SCI-3 and SCMS-30 (413 K, 30 min., $C_{\text{stabilizer}} = 0.2$ mass%)

*Stabilizer**	*PPI*	
	SCI-30	*SCMS*-30
1	75	87
2	78	90
5	81	91
7	82	92
11	71	85
13	78	89
20	73	85
22	87	92
24	90	93
26	92	97
28	96	98
Ionol	66	–
Diphenylphenylendiamine	76	–
N-(2-hydroxybenzyl)-*N*-(2-hydroxy-3-oxylbenzyl) amine (BTC-1)	–	82

* The number of stabilizer corresponds to the number of compound in Table V.

TABLE XII The influence of pyranylaminophenols on thermooxidative stability of industrial oils, PP and PVC (448 K, $C_o = 3 \cdot 10^{-3}$ mol/kg)*

Compound	*Oil I*-40		*PP*		*PVC*	
	τ, *min*	τ_{sc}/τ_o	τ, *min*	τ_{sc}/τ_o	τ', *min*	τ_{sc}/τ_o
without stabilizer	21	–	35	–	3	–
2-[*N*-(4-methyl-5, 6-dihydro-2Hpyranyl-5)amino]phenol	135	6.4	196	5.6	26	8.7
4-[*N*-(4-methyl-5, 6-dihydro-2H-pyranyl-5)amino]phenol	130	6.2	190	5.4	28	9.3
4-[*N*-phenyl-*N*-(4-methyl-5, 6-dihydro-2H-pyranyl-5)amino]phenol	45	2.1	–	–	32	10.6
2-oligoisobutylenyl-4-[*N*-phenyl-*N*-(4-methyl-5,6-dihydro-2H-pyranyl-5)amino]phenol	200	9.5	315	9.0	–	–
3-(4-methyl-5,6-dihydro-2H-pyranyl-5)-2-	176	8.4	190	5.4	27	9.0
3-(4-methyl-5,6-dihydro-2H-pyranyl-5)-4(*N*-phenyl)aminophenol	165	7.7	–	–	32	10.6
3-(4-methyl-5,6-dihydro-2H-pyranyl-5)-4(*N*-phenyl)aminophenol	65	3.1	–	–	–	–
2-oligoisobutylenyl-5(-4-methyl-5,6-dihydro-2H-pyranyl-5)-4-(*N*-phenyl) aminophenol	250	11.9	320	9.1	28	9.3
4-oxydiphenylamine	130	6.2	200	5.7	6	2
2,6-di-tertbutylphenol	–	–	–	–	9	3

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