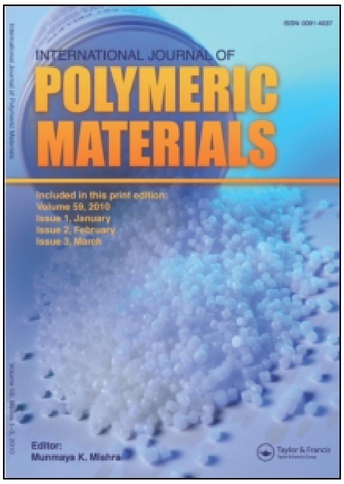


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Synthesis of New Stabilizers Through Polymer-Analogous Conversions

R. Z. Biglova[a]; V. P. Malinskaya[a]; G. E. Zaikov[b]; K. S. Minsker[a]
[a] Bashkirian State University, Ufa, Moscow, Russia. [b] Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia.

To cite this Article Biglova, R. Z. , Malinskaya, V. P. , Zaikov, G. E. and Minsker, K. S.(1994) 'Synthesis of New Stabilizers Through Polymer-Analogous Conversions', International Journal of Polymeric Materials, 24: 1, 151 — 156
To link to this Article: DOI: 10.1080/00914039408028561
URL: http://dx.doi.org/10.1080/00914039408028561

Intern. J. Polymeric Mater., 1994, Vol. 24, pp. 151–156
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

Synthesis of New Stabilizers Through Polymer-Analogous Conversions

R. Z. BIGLOVA, V. P. MALINSKAYA, G. E. ZAIKOV* and K. S. MINSKER

*Bashkirian State University, Ufa-450076, Frunze Street 32; *Institute of Chemical Physics, Russian Academy of Sciences, 4, Kosyguin Street, Moscow-117334, Russia.*

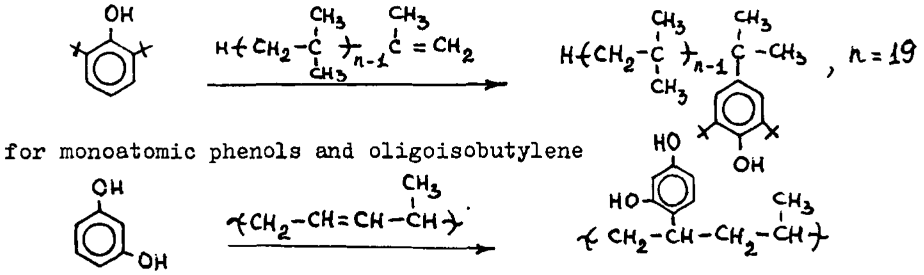
The polymer-analogous reaction provides an opportunity for the synthesis of new non-toxic and highly effective additives that solve the problems of mono- and diatomic phenols.

KEY WORDS Macromolecular stabilizers

Traditional antioxidants, which are used for the stabilization of polymers against thermooxidative degradation, are easily evaporated during industrial processing, are insufficiently compatible with a polymer, or are extracted by water or organic solvents under operating conditions.

The polymer-analogous reaction provides opportunities for the synthesis of new non-toxic and highly effective chemical additives for polymers which do not have the above shortcomings.

Commercial mono- and diatomic phenols, various aminophenols as well as by-products of a number of polymer production processes, for instance, of isobutylene, polyethylene, polypropylene, were used for the stabilizer synthesis. The alkylation of mono- and diatomic phenols by α-olefin oligomers (ethylene, propylene, isobutylene) or dienes (piperylene) to the aromatic ring in the presence of a catalytic quantity of complex aluminium salts proceeds according to the following scheme:



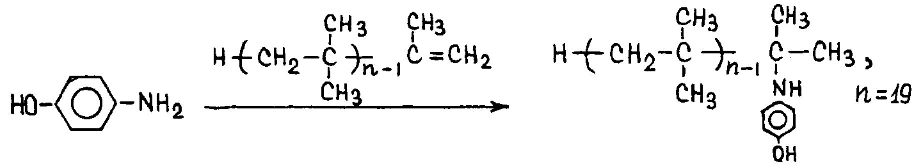
for monoatomic phenols and oligoisobutylene

for diatomic phenols and the oligopiperylene chain.

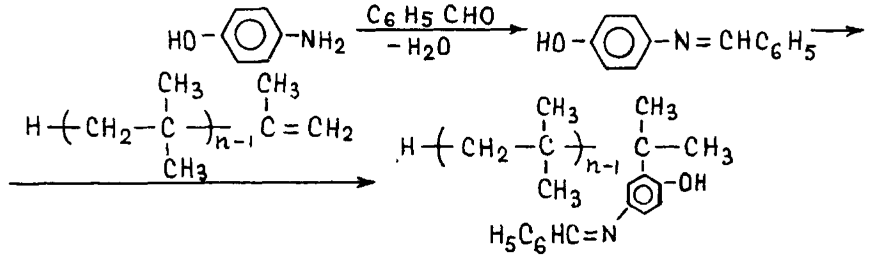
The total mesomeric increase in electrophilic substitution in the benzene ring that is caused by an hydroxyl group allows ready reaction with weak electrophiles. For diatomic phenols this reactivity increase is even more expressed. Therefore the above processes proceed during unprolonged heating of the original substances in a limited hydrocarbon medium with a yield, which is near quantitative. (For monoatomic phenols at 110–120°C, for diatomic ones at 80–100°C).

The number of phenol fragments, included into a polymer chain, was defined through the correlation of an ozonometric determination of double bonds in the original polymer and a quantitative determination of the hydroxy-groups in the alkylated product, using the titration by Verley.[1]

The aminophenol alkylation was carried out in a similar way, the original aminophenol having the aminogroup replaced.



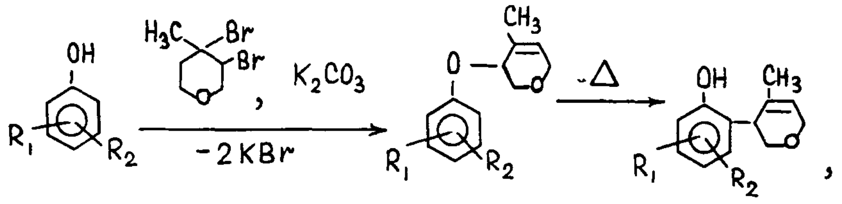
With the purpose of obtaining a number of aminophenols alkylated on the benzene ring the original aminophenols were preliminary turned into Schiff's bases through a reaction with benzaldehyde. The reactions with various oligomers were carried out after that. The structure of the synthesized compounds was proved using IR- and NMR ^{13}C-spectroscopy.



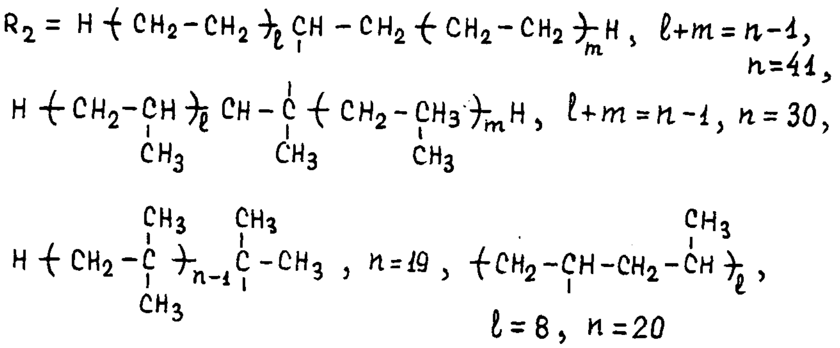
Oligomeric phenols may be used to carry out further polymer-analogous conversions. For instance, in the condensation of alkylated phenols with 3,4-dibrom-I-methyltetrahydropyran (obtained from the waste of dioxane-pyran production) synthesized a number of phenyl ethers, which in the presence of N,N-diethylaniline are exposed to Claisen rearrangement to form oligomeric (4-methyl-5,6-dihydro-2H-pyranil) phenols with high regiospecificity and quantitative yield. Both for para- and ortho-alkylated phenyl ethers the Claisen ortho-rearrangement exclusively takes place despite the steric difficulties created by the volumetric oligomer radical in the ortho-position of the benzene ring.

Depending on the nature and position of an oligomeric substituent phenyl ethers are differentiated by the ease of pyranyl radical migration to the benzene ring. Thus, the pyranyl radical migration proceeds more easily over the transition from oligoethylene to oligoisobutylene and oligopropylene.

The polymer-analogous conversions of oligomer diatomic phenols, were of special interest and caused certain difficulties due to the necessity to protect one of hydroxy-groups from formation of ortho-phenyl ethers with subsequent rearrangement. For this purpose oligomer-alkylated diatomic phenols are benzoylated (the



$R_1 = H$, $2-CH_3$, $4-CH(CH_3)_2$;

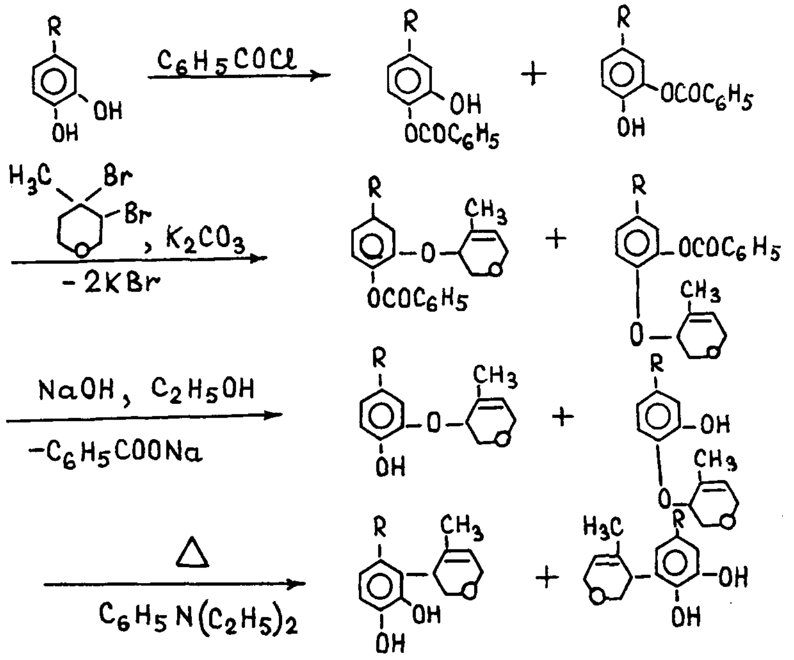


$$R_2 = H\left(CH_2-CH_2\right)_{l}\underset{|}{C}H-CH_2\left(CH_2-CH_2\right)_{m}H, \quad l+m=n-1, \quad n=41,$$

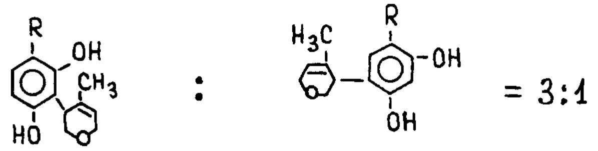
$$H\left(CH_2-\underset{CH_3}{CH}\right)_{l}CH-\underset{CH_3}{\overset{|}{C}}\left(CH_2-\underset{CH_3}{CH_3}\right)_{m}H, \quad l+m=n-1, \quad n=30,$$

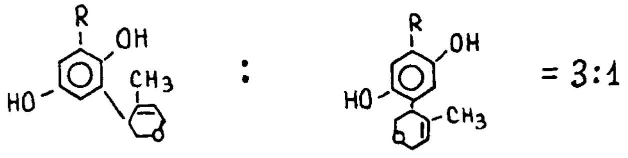
$$H\left(CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right)_{n-1}\overset{CH_3}{\underset{|}{C}}-CH_3, \quad n=19, \quad \left(CH_2-\underset{|}{C}H-CH_2-\overset{CH_3}{CH}\right)_{l}, \quad l=8, \quad n=20$$

ratio of phenols to benzoylchloride is 1.0:0.5) and then are condensed with 3,4-dibrome-4-methyl-tetrahydropyran. The obtained ortho-phenyl ethers, after hydrolysis of the protecting group, undergo regrouping into oligomer diatomic dihydropyranyl-phenols according to the following scheme:



The structures and yields of the synthesized products have been established by ^{13}C NMR-spectroscopy using the correlation of integration curves of the carbon signals in the benzene ring connected to the high molecular weight radical. In the case of pyrocatechol-based substances the isomer ratio is 1:1, for resorcinol- and hydroquinone is 3:1.





Testing of the synthesized compounds in real polymer formulations showed that they were characterized by a wide spectrum of stabilizing effects.

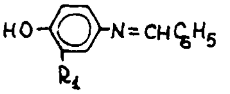
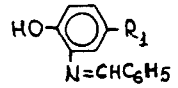
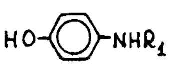
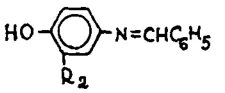
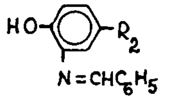
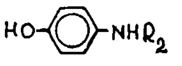
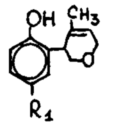
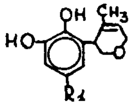
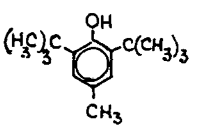
One may observe, that the addition of the poly-α-olefin-phenol to PVC samples slows down the dehydrochlorination process, improves the colour stability of the polymer and makes it easier to process the material due to an increase of the melt index (Table I). The stabilizing efficiency of macromolecular antioxidants depends on both the nature of the phenol and the polymer radicals. For diatomic phenols the effectiveness is higher, than for the monoatomic phenols. Effectiveness relates to variations in the polymer radical also: polyethylene < polypropylene < polyisobutylene.

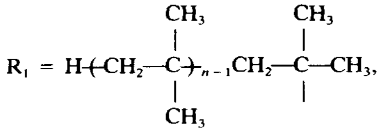
The presence of a polar heterocyclic substituent (4-methyl-5,6-dihydro-2H-pyranyl) in the oligomeric phenol molecule improves compatibility with PVC and increases lubricating effects. The compositions have been characterized by a large thermal stability period (τ = 54, for a concentration of 1 m.p.), that is obviously connected with the HCl linking on the double bond of a pyranyl radical. This allows partial substitution of, and in some cases to quite give up completely metal-containing stabilizers.

Oligomeric phenols and aminophenols proved to good in the halogen containing rubber formulations (CPE, EPC, CEPC, CEPCT). They extend the thermal stability of the composition by 2 or 3 fold compared to low molecular weight antioxidants, and considerably improve their physical and mechanical properties. In particular, the data given in Table I show that the introduction of 1.0 m.p. of oligomeric additive to a compositions based on chlorcontained rubbers not only increased the thermal stability and improved the colour stability, but also effected such physical/ mechanic indices as relative lengthening, frost resistance and wearability.

TABLE I

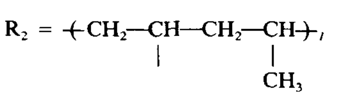
The macromolecular antioxidants effect on thermal and colour stability of halogen-containing polymers

NN	Antioxidant, C = 1 m.p.	PVC τ, min. (175 C) colour, b	CPE τ, min. colour, b	CEPC τ, min. colour, b	CSPE τ, min. colour, b	CI τ, min. (130 C) colour, b
1.		41 2.0	40 2.0	31 2.5	27 2.5	—
2.		42 2.0	39 2.0	33 2.0	28 2.5	—
3.		40 2.0	42 2.0	35 2.0	28 3.0	—
4.		44 1.5	45 2.0	—	33 2.0	123 (CL)
5.		45 1.5	44 2.0	—	34 2.0	110 (CL)
6.		43 1.5	45 1.5	39 1.5	30 2.0	—
7.		54 1.5	58 1.5	—	47 1.5	—
8.		79 1.5	61 1.5	—	51 1.5	—
9.		20 4.5	24 4.5	20 4.5	17 5.0	80 (CL)



$$R_1 = H\text{-}\!\left(CH_2-\underset{CH_3}{\overset{CH_3}{C}}\right)_{n-1}CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3,$$

n = 19



$$R_2 = \left(CH_2-\underset{|}{CH}-CH_2-\underset{CH_3}{CH}\right)_l,$$

l = 8, n = 20

In the synthesis of new stabilizers the ecological and economic aspects should be considered as well. In connection with the above the proposed compounds possess great prospects, since they are made from raw byproduct oligomers from polymerization processes. This allows us to simultaneously solve the problem of the synthesis of effective non-toxic stabilizers with complex action, and the utilization of raw byproducts.