Synthesis of New Stabilisers through Polymer-analogous Conversions

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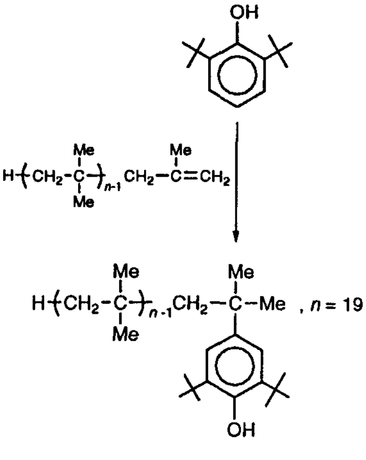
Polymer-analogue reactions of poly-α-olefins and polydiene with phenols and aminophenols lead to the formation of stabilisers of halogenated polymers.

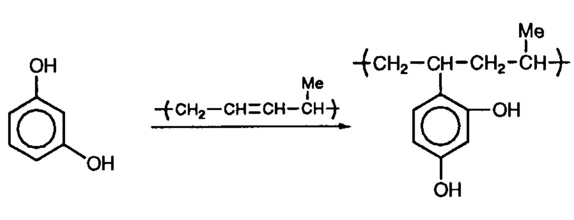
Polymer-analogue reactions make it possible to synthesise new, non-toxic and highly effective chemical additives to polymers.

Commercially available monohydric and dihydric phenols, various aminophenols and non-standard products as well as side products from a number of polymer industries, for example, polyisobutylene ($M_w/M_n = 1.4$, $M_n = 1100$, $n = 19$), polyethylene ($M_w/M_n = 1.4$, $M_n = 1500$, $n = 53$), polypropylene ($M_w/M_n = 1.1$, $M_n = 1400$, $n = 33$), polyisoprene (oligopiperylene $M_w/M_n = 2.0$, $M_n = 1400$, $n = 20$, average number of double bonds per macromolecule $l = 8$) were used to synthesise the stabilisers. This made it possible to solve simultaneously the problem of the synthesis of effective stabilisers having a combined activity and of the utilisation of non-standard products. The alkylation of monohydric and dihydric phenols by α-olefin (ethylene, propene, isobutene) or diene (piperylene) oligomers in the aromatic ring in the presence of Na[AlCl$_4$] as a catalyst has been carried out in accordance with reaction (1):



(1)

for monohydric phenols and oligoisobutylene and reaction (2):

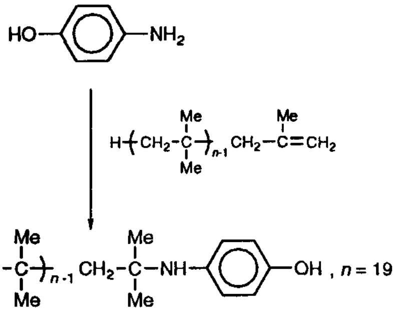


(2)

for dihydric phenols and the oligopiperylene unit.

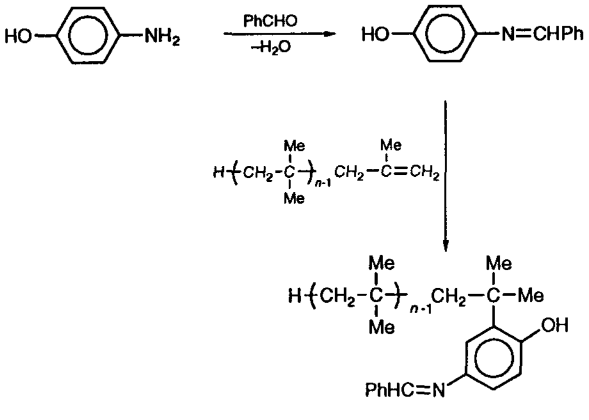
The above processes occurred on brief heating of the starting materials in saturated hydrocarbons with nearly quantitative yields (at 110–120 °C for monohydric phenols and at 100–110 °C for dihydric phenols). The number of phenolic fragments which had entered into the polymer chain was established by comparing the results of the ozonometric determination of C = C double bonds in the initial oligomer and the quantitative determination of the hydroxy groups in the alkylated product by titration.

The alkylation of aminophenols was carried out similarly, reaction (3). The reaction of the initial aminophenol involves the amino-group.



(3)

In order to obtain a series of aminophenol derivatives alkylated in the aromatic ring, the aminophenols were first converted into Schiff bases by reaction with benzaldehyde, after which the reactions with various oligomers were carried out, Scheme 1.



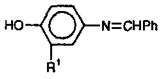
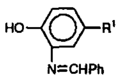
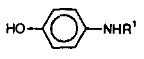
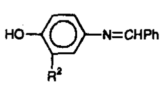
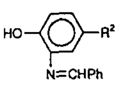
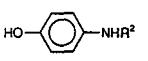
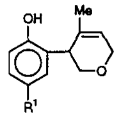
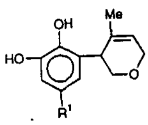
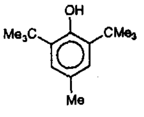
Scheme 1

Oligomeric phenols may serve as a basis for futher polymer-analogue reactions. For example, the condensation of alkylated phenols with 3,4-dibromo-1-methyltetrahydropyran (obtained from pyran, a waste product in the industrial production of dioxane) led to the synthesis of a series of phenyl ethers, which

Table 1 ^{13}C NMR spectroscopic data for (4-methyl-5,6-dihydro-2*H*-pyranyl)polypropenyldihydroxybenzenes.

No.	Compound	δ(ppm), singlet
1	3-(4-Methyl-5,6-dihydro-2*H*-pyranyl)-5-polypropylenyl-1,2-dihydroxybenzene	122.5
2	3-(4-Methyl-5,6-dihydro-2*H*-pyranyl)-4-polypropylenyl-1,2-dihydroxybenzene	139.7
3	2-(4-Methyl-5,6-dihydro-2*H*-pyranyl)-4-polypropylenyl-1,3-dihydroxybenzene	128.6
4	4-(4-Methyl-5,6-dihydro-2*H*-pyranyl)-6-polypropylenyl-1,3-dihydroxybenzene	129.6
5	3-(4-Methyl-5,6-dihydro-2*H*-pyranyl)-5-polypropylenyl-1,4-dihydroxybenzene	137.3
6	2-(4-Methyl-5,6-dihydro-2*H*-pyranyl)-5-polypropylenyl-1,4-dihydroxybenzene	134.8

Table 2 The influence of high molecular mass antioxidants on the thermal stability and colour fastness of halogen-containing polymers (175 °C)[a]

		PVC		CPE		CEPR		CSPE	
No.	Antioxidant,[b] $C = 1$ ppm	τ/min	Colour, scale points	τ/min	Colour, scale points	τ/min	Colour, scale points	τ/min	Colour, scale points
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	—	—	35	2.0
5		45	1.5	44	2.0	—	—	34	2.0
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

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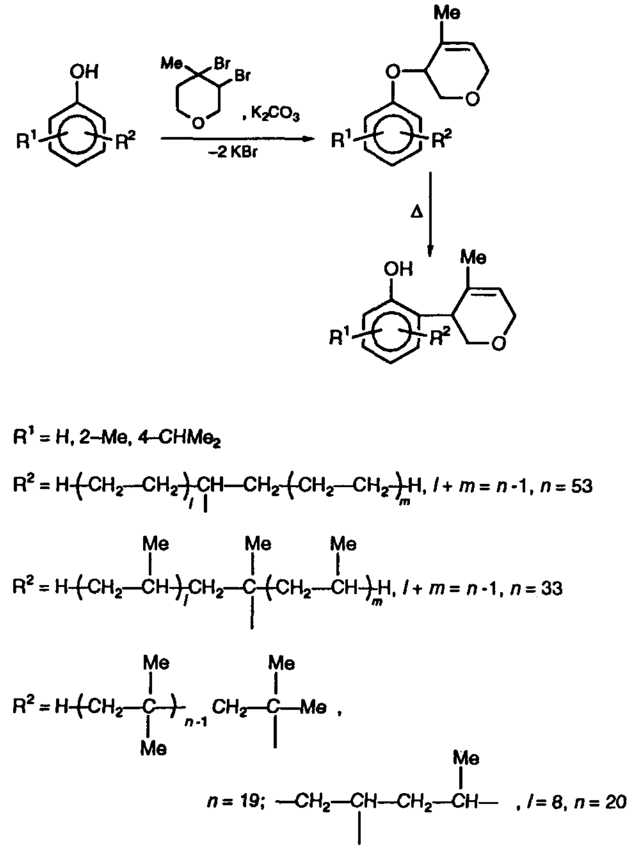
[a] The duration of thermal stability (τ/min) and the colour fastness (points on the Synmero scale) were determined as described by Ocsay *et al.*[2]
[b] $R^1 = H(CH_2CMe_2)_{n-1}CH_2C(Me_2)-$, $R^2 = -(CH_2CHCH_2CHMe)_l-$.



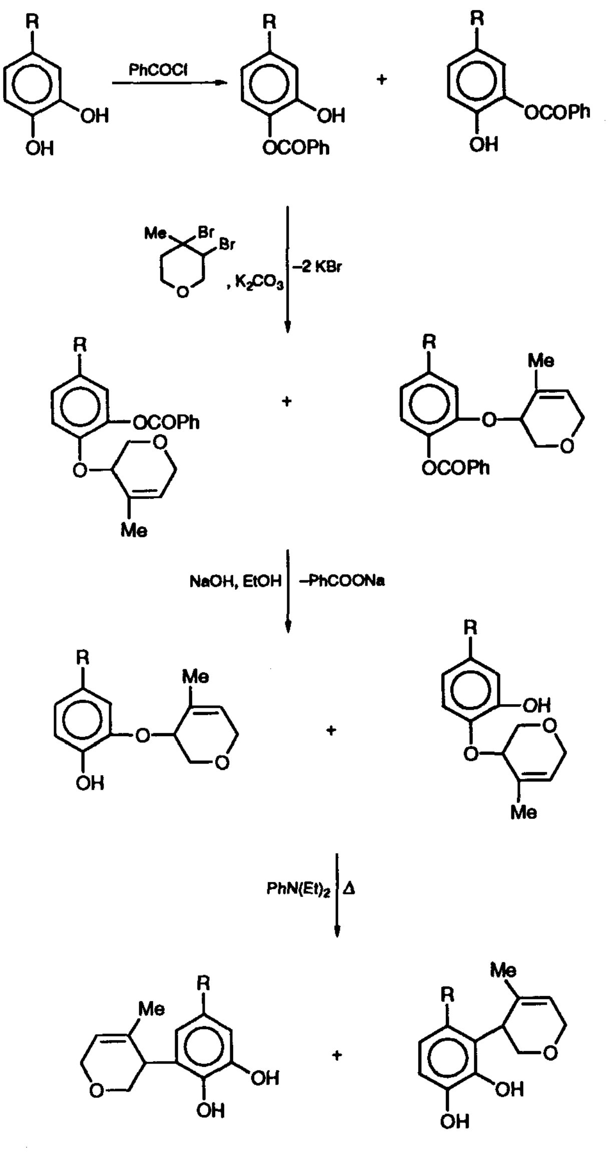
Scheme 2

were subjected to the Claisen rearrangement in the presence of *N*,*N*-diethylaniline to oligomeric (4-methyl-5,6-dihydro-2*H*-pyranyl)phenols with a high regiospecificity and in quantitative yields. The Claisen *ortho*-rearrangement takes place for both *para*- and *ortho*-alkylated phenyl ethers despite the steric hindrance generated by the bulky oligomeric group in the *o*-position in the aromatic ring,[1] Scheme 2.

The possibility of introducing the dihydropyranyl fragment into the molecules of dihydric phenols is noteworthy. The process proceeds *via* a stage in which one of the hydroxy-groups is protected, this being followed by condensation with 3,4-dibromo-4-methyltetrahydropyran in accordance with Scheme 3, where R is an oligomeric group.

The structure of the products synthesised was established from the ^{13}C NMR spectra. Table 1 presents the chemical shifts of the aromatic ring carbon atom linked to the oligomeric group in (4-methyl-5,6-dihydro-2*H*-pyranyl)polypropylenyldihydroxybenzenes. The isomer ratio is 1:1 for compounds based on catechol and 3:1 for those based on resorcinol and hydroquinone, *i.e.* 2-(4-methyl-5,6-dihydro-2*H*-pyranyl)-4-polyolefinyl-1,3-dihydroxybenzene:4-(4-methyl-5,6-dihydro-2*H*-pyranyl)-6-polyolefinyl-1,3-dihydroxybenzene = 3:1 and 3-(4-methyl-5,6-dihydro-2*H*-pyranyl)-5-polyolefinyl-1,4-dihydroxybenzene:2-(4-methyl-5,6-dihydro-2*H*-pyranyl)-5-polyolefinyl-1,4-dihydroxybenzene = 3:1.

Tests on those compounds synthesised specified in the recipes for polymeric materials showed that they exhibit a wide range of stabilising activities. After their introduction into PVC, polyolefinylphenols retard the dehydrochlorination process and improve the thermal stability and colour fastness of the polymer (Table 2). The presence of a polar heterocyclic substituent (4-methyl-5,6-dihydro-2*H*-pyranyl) in the oligomeric phenols significantly increases the efficiency of the stabiliser, increasing the duration of the thermal stability of the polymer, which can apparently be caused by the addition of HCl to the double bond of the pyranyl group.



Scheme 3

All the stabilisers synthesised have also proved to be very useful in the recipes for halogenated raw rubbers: chlorinated ethylene–propene rubber (CEPR), chloropolyethylene (CPE), chlorosulfopolyethylene (CSPE) and chlorinated ethylene–propene ternary rubber (CEPTR). They impart to the compositions a duration of thermal stability greater by a factor of 2–3 than low molecular mass antioxidants (Table 2).

References

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