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BRIEF COMMUNICATIONS

Calix[4]resorcinols as Stabilizers for Rubber Stocks Based on Butadiene–Acrylonitrile Rubbers

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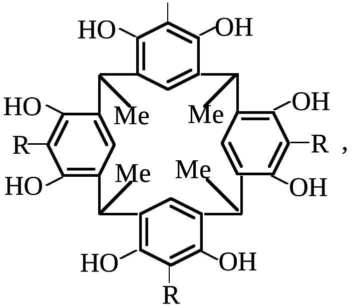
Abstract—Modification of tetramethylcalix[4]resorcinol with dimethylaminomethyl and 3,5-di-*tert*-butyl-4-hydroxybenzyl fragments was studied. The antioxidative activity of these macrocyclic stabilizers in rubber stocks based on butadiene–acrylonitrile rubber was examined.

Phenolic stabilizers are relatively little used in rubber stocks, as they are apparently inferior in the protective effect to *p*-phenylenediamine derivatives. At the same time, a major advantage of phenolic stabilizers is that, in contrast to amines, they do not alter or alter only slightly the color of rubber items; also, they are nontoxic and low-volatile and are difficultly washed out.

Macrocyclic phenolic stabilizers, in particular, calix[4]resorcinols, are a new group of phenolic stabilizers. Tetramethylcalix[4]resorcinol **I** appeared to be suitable as antioxidant for vulcanized rubbers based on butadiene–acrylonitrile rubbers [1, 2].

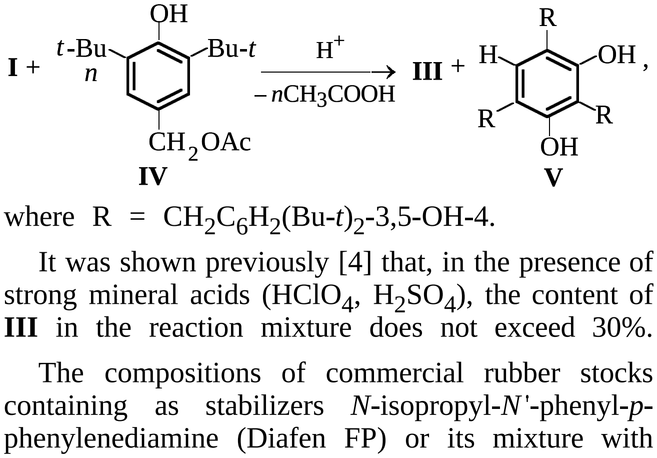
In this work we studied the antioxidative activity exhibited in rubber stocks based on butadiene–acrylonitrile rubbers by modified tetramethylcalix[4]resorcinols **II** and **III** containing in *o*-positions of the aromatic rings dimethylaminomethyl or 3,5-di-*tert*-butyl-4-hydroxybenzyl fragments:



where R = H (**I**), CH_2NMe_2 (**II**), or $CH_2C_6H_2(Bu\text{-}t)_2$-3,5-OH-4 (**III**).

It is known that introduction of dimethylaminomethyl groups into the molecule of **I** appreciably facilitates its oxidation [3]. Therefore, compound **II** should be a much more effective trap of peroxy radicals, compared to unsubstituted calixarene **I**.

Compound **III** contains phenolic groups differing in the reactivity. This should enhance the inhibiting performance in radical oxidation processes. Stabilizer **III** was prepared by the reaction of **I** with 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate **IV** in the presence of formic acid. The mixture formed in the course of the reaction contains 70% calixarene **III** and 30% 2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)resorcinol **V**:



IV **V**

where R = $CH_2C_6H_2(Bu\text{-}t)_2$-3,5-OH-4.

It was shown previously [4] that, in the presence of strong mineral acids ($HClO_4$, H_2SO_4), the content of **III** in the reaction mixture does not exceed 30%.

The compositions of commercial rubber stocks containing as stabilizers *N*-isopropyl-*N*'-phenyl-*p*-phenylenediamine (Diafen FP) or its mixture with 2,2,4-trimethyl-1,2-dihydroquinoline (Acetonanil),

Table 1. Composition of rubber stocks based on SKN-18 and SKN-26 rubbers

Component*	Content, wt parts per 100 wt parts of rubber	
	SKN-18	SKN-26
Zinc oxide	4	3
Sulfenamide Ts	1	0.7
N,*N*-Dithiodimorpholine	2	–
Thiuram D	1	–
Stearic acid	1	1
Carbon black	120	40
EDOS plasticizer	45	–
Sulfur	–	1.5
Stabilizer	4	2

* Sulfenamide Ts is *N*-cyclohexyl-2-benzothiazolylsulfenamide; Thiuram D, tetramethylthiuram disulfide; EDOS plasticizer, a mixture based on dioxane alcohols; stabilizer, compounds **I**–**III**, **V**, **III** + **V**, Diafen FP, or Acetonanil.

calixarenes **I**–**III**, benzylated resorcinol **V**, and a mixture of **III** and **V** obtained in the course of the reaction of **I** with **IV** are listed in Table 1. The results of physicomechanical tests of these stocks are listed in Table 2. The performance of the stabilizers was evaluated by relative changes in the nominal tensile strength σ, relative elongation at break ε, and elongation set θ, occurring upon thermal oxidative aging.

Table 2 shows that, in the rubber stock of thiuram vulcanization with a high filler content, modified calixarenes **II** and **III** somewhat surpass **II** and Diafen FP (amine stabilizers) as regards preservation of σ, but are inferior to the latter additives with respect to preservation of ε. In the rubber stock of sulfur vulcanization with a low filler content, exhibiting better physicomechanical properties, calixarenes **II** and **III** inhibit thermal oxidative degradation more effectively than **I** and are comparable in this respect with Diafen FP (Table 2).

EXPERIMENTAL

In our study, we used commercial samples of butadiene–acrylonitrile rubbers SKN-18 and SKN-26. Rubber stocks were prepared in two steps with a Brabender plasticorder with the mixing chamber volume of 50 cm^3. In the first step, the rubber, carbon black, and other components, except the vulcanizing group, were mixed at 130°C. In the second step, the vulcanizing group was added. The total mixing time was 7 min, and the rotor rotation rate, 35 rpm. The rubber stocks based on SKN-18 and SKN-26 were vulcanized at 143°C for 30 and 40 min, respectively.

Physicomechanical tests were performed with a Tensometer T-10 tensile-testing machine (Monsanto).

The ^{1}H NMR spectra were recorded on a Varian Gemini-200 spectrometer (200 MHz) relative to residual protons of deuterated solvents.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,19-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene III. Formic acid (65 ml) was added to a solution of 3 g (5.5 mmol) of **I** and 6.9 g (24.8 mmol) of **IV** in 55 ml of acetone. The mixture was allowed to stand at 20°C for 1 day. Then it was poured into 100 ml of water, and an NaHCO$_3$ solution was added to pH 5–6. A mixture of products (7.75 g) was obtained, containing, according to the ^{1}H NMR spectrum, compounds **V** and **III** in a molar ratio of 3 : 7. It was dissolved in 25 ml of benzene, and 170 ml of hexane was added. Compound **III** was obtained; yield

Table 2. Effect of stabilizers on properties of vulcanized rubbers based on SKN-18 and SKN-26

Parameter	Stabilizer					
	control*	**I**	**II**	**III**	**V**	**III** + **V**
σ, MPa	14.0 (21.2)**	13.7 (23.5)	13.3 (18.0)	12.7 (20.1)	13.2 (20.5)	14.7 (21.6)
ε, %	129 (314)	148 (320)	117 (244)	133 (308)	156 (310)	129 (280)
θ, %	4 (8)	3 (9)	4 (8)	4 (8)	4 (10)	3 (8)
ε'/ε***	0.89 (0.87)	0.89 (0.78)	0.94 (1.06)	0.91 (0.95)	0.81 (0.95)	0.89 (0.88)
θ'/θ***	0.95 (0.69)	0.98 (0.60)	0.75 (0.82)	0.80 (0.62)	0.81 (0.77)	0.62 (0.69)

* For vulcanized rubber based on SKN-18, Diafen FP : Acetonanil (1 : 3); for that based on SKN-26, Diafen FP.

** The values for SKN-26 are given in parentheses.

*** (ε', θ') Values obtained after thermal oxidative aging at 100°C for 72 h.

2.6 g (33%), mp 230°C (dec.). ^{1}H NMR spectrum CDCl$_3$), δ, ppm: 1.39 s (72H, CMe$_3$), 1.77 d (12H, Me, $^3J_{HH}$ 7.0 Hz), 3.89 s (8H, CH$_2$), 4.60 q (4H, CH, $^3J_{HH}$ 7.0 Hz), 5.08 s (4H, OH), 6.34 s (8H, OH), 7.00 s (8H, Ar–H), 7.33 s (4H, Ar–H).

Found, %: C 77.65; H 8.65.
$C_{92}H_{120}O_{12}$.
Calculated, %: C 77.97; H 8.47.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,19-tetrakis(dimethylaminomethyl)-2,8,14,20-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene II and 2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)resorcinol V were prepared as described in [5] and [6], respectively.

CONCLUSION

Modification of tetramethylcalix[4]resorcinol with dimethylaminomethyl and 3,5-di-*tert*-butyl-4-hydroxybenzyl fragments afforded macrocyclic stabilizers with enhanced antioxidative activity, exceeding that of the starting tetramethylcalix[4]resorcinol, toward rubber stocks based on butadiene–acrylonitrile rubbers.

ACKNOWLEDGMENTS

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