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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Styrylation of Phenol in the Presence of Cation-Exchange Resins. Influence of the Product Composition on Its Stabilizing Performance in Rubber

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Abstract—Methylbenzylated phenols were prepared by catalytic reaction of phenol with styrenes. The effect of a series of cation-exchange resins on the product composition was examined, and the stabilizing performance of the products in rubber was evaluated.

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Alkyl(aryl)phenols, including methylbenzylated phenols (MBPs), are widely used in polymer chemistry as antioxidant additives. The commercial procedure for preparing these compounds is the reaction of phenol with styrene or α-methylstyrene, catalyzed by mineral or organic acids under homogeneous conditions [1]. The reaction product is a mixture of mono-, di-, and trisubstituted MBPs of various structures [2].

However, performing the reaction in the presence of a homogeneous catalyst makes it necessary to wash the product to remove the catalyst, which results in formation of a large amount of wastewater. This fact strongly impedes introduction of MBPs into the practice of polymer stabilization [3].

Among recent studies on synthesis of arylaklyl-substituted phenols, we should particularly mention studies performed with heterogeneous catalysts [4, 5]. In this case, the catalyst can be readily separated from the reaction mixture; furthermore, it can be reused.

In this study we examined the influence of structural characteristics of cation-exchange resins on the composition of the product formed in the reaction of phenol with styrene. We also examined how the composition of the resulting MBP correlates with its stabilizing performance.

EXPERIMENTAL

The starting substances were phenol [GOST (State Standard) 23519–93; mp 40.9, bp 182°C; d^{20} 1.0576 g cm^{-3}] and styrene (GOST 1003–93; bp 145.2°C, d^{20} 0.9060 g cm^{-3}). The thermal polymerization inhibitor was 2,6-di-*tert*-butyl-4-methylphenol (GOST 28584–90, mp 70°C). The catalysts were KU-23 (GOST 20298–74), Lewatit K-2629 and K-2431 (Bayer), and Purolite CT-151 (Purolite). The stabilizing effect was examined with SKI-3 isoprene rubber (GOST 14925–79).

The progress of the reaction of phenol with styrene was monitored by gas–liquid chromatography (GLC) with a Waters 440 device equipped with a μBondapak C^{18} column 4 mm i.d. The eluent was acetonitrile, flow rate 1 ml min^{-1}. Methylbenzylated phenols were detected by UV absorption at 265 nm, sensitivity 1.28 absorption units for the whole scale.

The induction period of rubber oxidation was determined by the standard procedure [6].

The kinetics of accumulation of carbonyl groups in the course of thermal oxidation of SKI-3 rubber was studied by IR spectroscopy with a UR-75 device. As analytical band we used the absorption band at 1721 cm^{-1} corresponding to stretching vibrations of the >C=O group.

Variation of the molecular weight of the polymer in the course of thermal oxidation was monitored by viscometry [7]. To characterize the rubber stability in the course of thermal oxidation, we used the degradation coefficient K_d

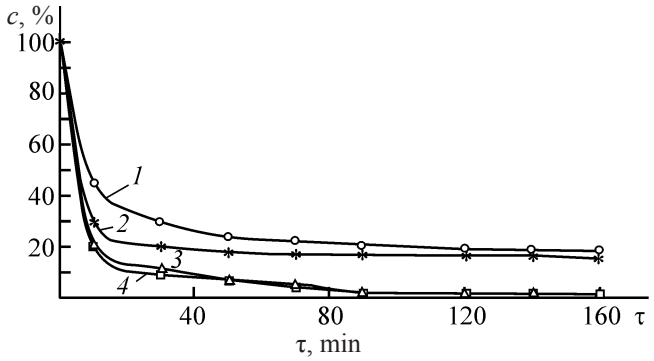

Fig. 1. Amount of phenol *c* in the reaction mixture as a function of time τ at various component ratios. Catalyst Lewatit K-2431, temperature up to 130°C. Phenol : styrene molar ratio: (*1*) 1 : 1, (*2*) 1 : 1.5, (*3*) 1 : 1.7, and (*4*) 1 : 2.

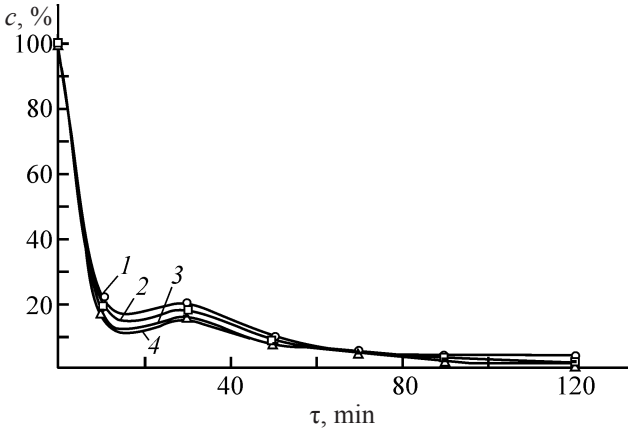

Fig. 2. Amount of phenol c in the course of styrylation as a function of reaction time τ. Amount of Lewatit catalyst, %: (*1*) 10, (*2*) 15, (*3*) 20, and (*4*) 25.

$$K_{d.} = 1/[\eta]_{ox} - 1/[\eta]_{in},$$

where $[\eta]_{ox}$ is the viscosity of the oxidized sample, and $[\eta]_{in}$, that of the initial sample.

A round-bottomed flask equipped with a thermometer, a stirrer, and a reflux condenser was charged with phenol (1 mol), catalyst (10–25 wt % relative to phenol), and inhibitor of styrene polymerization (0.0016 mol). The flask was heated to 90°C, and styrene was gradually added (1 mol). Then, in the course of further dropwise addition of the remaining styrene (0.7–1 mol), the temperature in the flask was gradually elevated to 130°C. In the course of the reaction, samples were taken at preset intervals for the analysis. The reaction was considered complete if the phenol concentration in the reaction mixture ceased to change. The heterogeneous catalyst was filtered off, and the unchanged phenol was distilled off at 30 mm Hg with live steam.

Table 1. Influence of the reactant ratio on the residual phenol content in the product. Catalyst Lewatit K-2431 (20 wt % relative to phenol), reaction time 120 min

Phenol : styrene molar ratio	Phenol content in product, %
1:1	19.53
1:1.5	15.96
1:1.7	2.00
1:2	2.01

Table 2. Content of methylbenzylated phenols at various amounts of Lewatit K-2431 catalyst. Reaction time 130 min

Catalyst amount, %	Content of substituted methylbenzylated phenols, %		
	mono-	di-	tri-
10	30.635	45.257	19.390
15	31.213	46.097	20.871
20	22.426	52.261	22.524
25	16.771	53.382	25.839

First we examined the influence of the reactant ratio on the rate of phenol consumption in the presence of various cation-exchange resins differing in the catalytic capacity and pore size. The methylbenzylation progress was judged from the amount of phenol in the reaction mixture, determined by GLC (Fig. 1).

We found that an increase in the amount of the methylbenzylating agent over 1.7 mol per mole of phenol does not lead to an increase in the reaction rate (Fig. 1) and to a decrease in the residual phenol content in the product (Table 1).

Then we examined the effect of the catalyst amount on specific features of phenol styrylation. The catalyst amount was varied from 10 to 25 wt % relative to phenol. We found that variation of the catalyst amount did not noticeably affect the rate of phenol consumption, but affected the product composition and residual phenol content (Fig. 2). An increase in the catalyst amount led to an increase in the content of di- and trisubstituted methylbenzylphenols (Table 2).

Further experiments were performed at a phenol : styrene molar ratio of 1 : 1.7. The catalyst amount was 20 wt % relative to phenol. We found that the structural characteristics of the cation-exchange resins affected

the rate of phenol conversion insignificantly (Fig. 3, Table 3). Only with KU-23 the rate of phenol consumption was somewhat higher. However, whereas in the presence of Lewatit K-2431, Lewatit K-2629, and Purolite CT-151 three compounds are formed, in the presence of KU-23 some other products detectable by GLC are also obtained (Table 4).

The use of different cation-exchange resins leads to different ratios of substituted phenols of various structures. The largest amount of disubstituted MBPs is formed by styrylation of phenol in the presence of Lewatit K-2629 (~43%). With Lewatit K-2431 resin characterized by smaller pore size, the di-MBP content was 39%, and the amount of mono-MBP increased. Purolite CT-151 shifts the process toward formation of trisubstituted MBPs, with the amount of di-MBPs decreasing to 35%. As Purolite CT-151 is characterized by the largest pore size, it is logical to assume that the catalyst pore size exerts a decisive effect on the product composition (Table 3).

The synthesized products **I–IV** differing in the chemical composition were tested as stabilizers for SKI-3 rubber.

As a qualitative express characteristic of the antioxidant performance we took the time before the start of oxygen uptake by the polymer in the course of thermal oxidation in an oxygen atmosphere at 155 ± 5°C. As a reference stabilizer we used commercial phenolic antioxidant Agidol 2, bis(2-hydroxy-5-methyl-3-*tert*-butylphenyl)methane.

Our results show that products **I–IV** make longer the induction period before the onset of rubber oxidation (Fig. 4). The kinetic curves of thermal oxidation of SKI-3 stabilized by products **I** and **II** which contain the largest amounts of disubstituted phenols show that the polymer is more stable than that stabilized by products **III** and **IV** containing appreciably smaller amounts of disubstituted MBPs. Apparently, an increase in the amount of disubstituted phenols leads to an increase in the stabilizer performance.

Table 3. Structural characteristics of the catalysts used

Characteristic	Catalyst			
	Lewatit K-2431	Lewatit K-2629	Purolite CT-151	KU-23
Specific surface area, $m^2\ g^{-1}$	19	18	20	20
Pore volume, $cm^3\ g^{-1}$	0.3	0.3	0.15	–
Effective pore diameter, nm	40	65–70	250	96
Total capacity, mg-equiv g^{-1}	1.1–1.2	1.8–1.9	5.1	4.8

As a quantitative criterion of the antioxidant performance of the synthesized MBPs we used an increase in the absorption intensity of the vibration band of carbonyl groups (1721 cm^{-1}) appearing in the course of thermal oxidation of SKI-3. As reference we used the optical density of the band at 1470 cm^{-1} belonging to bending vibrations of the $–CH_3$ and $–CH_2–$ groups.

As seen from Fig. 5, the rate of accumulation of carbonyl groups on adding stabilizers also depends on the composition of styrylation products. The experimental results are consistent with the kinetic curves of model thermal oxidation of SKI-3.

The induction period of polymer oxidation and the rate of accumulation of carbonyl groups allow

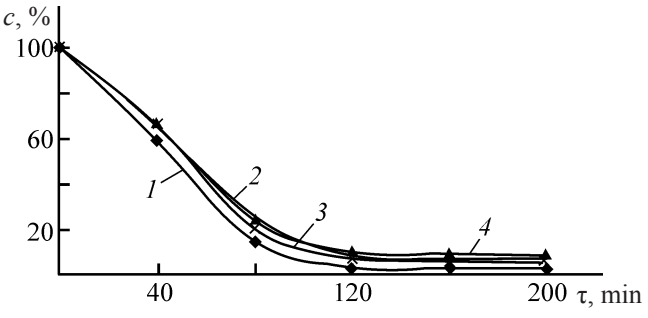

Fig. 3. Influence of the catalyst type on the rate of phenol consumption in the course of styrylation. Phenol : styrene molar ratio 1 : 1.7, 130°C, catalyst amount 20 wt % relative to phenol. (*c*) Phenol content and (τ) reaction time. Catalyst: (*1*) KU-23, (*2*) K-2629, (*3*) K-2431, and (*4*) CT-151.

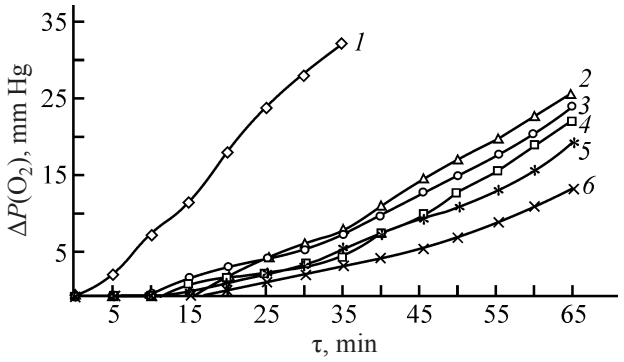

Fig. 4. Kinetic curves $\Delta P(O_2)$–τ of oxidation of SKI-3 containing various phenolic antioxidants. Initial $P(O_2)$ = 250 mm Hg, 150–160°C, c_{AO} = 0.3 wt %. Antioxidant: (*1*) none, (*2*) **IV**, (*3*) **II**, (*4*) I, (*5*) **III**, and (*6*) Agidol 2.

Table 4. Influence of the catalyst type on the composition of reaction products. Molar ratio phenol : styrene = 1 : 1.7, 130°C, 20 wt % catalyst relative to phenol

Catalyst	Product	Product composition, % (retention time, min)			
		mono- (3.33–3.50)	di- (3.80–3.83)	tri- (4.31–4.36)	other (4.50–4.80)
K -2629	**I**	28.99	42.95	16.73	–
K -2431	**II**	32.04	39.37	15.91	–
ST-151	**III**	32.29	35.20	22.86	–
KU-23	**IV**	26.29	16.54	18.55	34.02

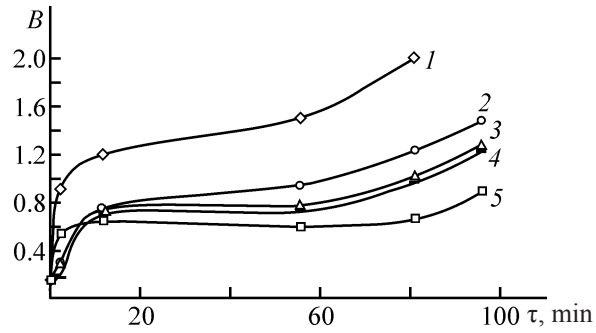

Fig. 5. Optical density of carbonyl absorption band at 1721 cm^{-1} relative to that at 1470 cm^{-1} ($B = D_1/D_2$) as a function of time τ of thermal oxidative aging of SKI-3 rubber films (air, 100°C). Antioxidant: (*1*) none, (*2*) **II**, (*3*) **IV**, (*4*) **III**, and (*5*) Agidol 2.

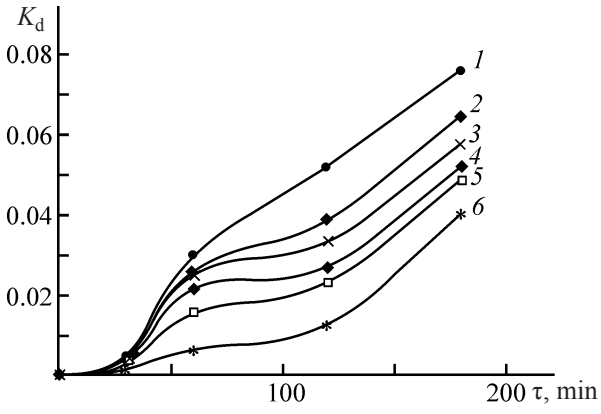

Fig. 6. Degradation coefficient of SKI-3 K_d with various antioxidants. c_{AO} = 0.3 wt %, thermal oxidation in air at 100°C. (τ) Time. Antioxidant: (*1*) none, (*2*) **IV**, (*3*) **I**, (*4*) **II**, (*5*) **III**, and (*6*) Agidol 2.

evaluation of the initial step of the polymer degradation. Deeper transformations can be judged from changes in the molecular weight of the polymer, responsible for physicomechanical properties of the polymeric material, in the course of degradation.

One of the most widely used methods for determining the molecular weight is measuring the viscosity of polymer solution. We estimated by viscometry the antioxidant performance of MBPs in SKI-3 rubber subjected to thermal oxidative aging in air at 130°C. To characterize the rubber stability, we used the degradation coefficient equal to the number of polymer chain breaks in a definite time of thermal oxidation (Fig. 6). With respect to the degradation coefficients, MBPs I and II containing the maximal amount of disubstituted products are on the same level with Agidol 2.

CONCLUSIONS

(1) The examined heterogeneous catalysts affect the composition of phenol styrylation products. The largest amount of disubstituted methylbenzylated phenols is formed with Lewatit K-2629 catalyst.

(2) The optimal molar ratio of phenol to styrene is 1 : 1.7.

(3) With an increase in the content of disubstituted methylbenzylphenols in the styrylation product, its antioxidant performance increases.

(4) With respect to the antioxidant performance in rubber, the product containing the maximal amount of disubstituted methylbenzylated phenols is on the same level with Agidol 2.

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