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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Acid-Catalyzed Alkenylation of Aromatic Compounds with 1,3-Pentadiene as a Route to New Modifying Additives for Polymer Compounds

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Abstract—Alkenylation of a series of aromatic compounds with 1,3-pentadiene was studied. The oligomeric alkenylation products cured with hexamethylenetetramine were used for modifying elastic-strength properties of elastomeric compounds and improving the compatibility of the elastomers with silicic acid fillers.

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The growing requirements to consumers' properties, service characteristics, and environmental safety of modern tires and general mechanical rubber goods call for development and application of new high-performance auxiliary ingredients, modifiers of polymer compounds considerably enhancing their strength. Phenolic compounds (resorcinol, 5-methylresorcinol) in combination with hexamethylenetetramine, widely used as modifying additives in formulations of rubber stocks and showing fairly high performance, have certain drawbacks [1].

As a continuation of previous studies [2–4] of acid-catalyzed alkenylation of shale resorcinols with 1,3-pentadiene (piperylene), it was interesting to further expand the range of aromatic compounds subject to alkylation with the aim to find new, more effective modifying additives to skimming rubber stocks based on general-purpose rubbers. Alkenylated derivatives introduced into an elastomeric matrix with the aim to improve the physicomechanical parameters of ready rubber items enhance the adhesion strength of rubber–metal cord systems under the conditions of steam and salt aging and positively affect the compatibility of rubbers with silicic acid fillers.

In this study, we examined the composition of alkylates formed by some aromatic compounds with 1,3-pentadiene under the conditions of phosphoric acid catalysis and evaluated the character and efficiency of the modifying action of the alkenylation products in polymer compounds.

EXPERIMENTAL

The following compounds were subjected to alkenylation with 1,3-pentadiene. Aromatic compounds with hydroxy group directly bonded to the aromatic ring: phenol, *p*-cresol, *p*-nonylphenol (Agidol 21, distilled, T grade), salicylic acid, a-naphthol, resorcinol, 5-methylresorcinol, and Alkirez-1 (a technical mixture of dihydric phenols mainly consisting of 5-methylresorcinol, 2,5-dimethyl-resorcinol, and their closest homologs); aromatic compounds containing no phenolic hydroxyls: styrene, a-methylstyrene, and benzoic acid.

The alkenylation was performed in the melt at 140°C. The molar ratio aromatic compound : 1,3-pentadiene : orthophosphoric acid was 1 : 2 : 0.1. The reaction was performed in two modes: (a) in the course of 5 h in a 30-cm^3 steel autoclave without forced stirring; (b) for 2–2.5 h in a 250 cm^3 glass vessel equipped with a power-driven stirrer, a dosing unit, and a reflux condenser. In the latter case, 1,3-pentadiene was added to the reaction mixture gradually in small portions.

The components were separated on a 30-m quartz capillary column coated with a nonpolar stationary phase, poly(methyl–5% phenyl)siloxane. In identification of the chromatographic peaks, we used along with the mass spectra the estimated boiling points and retention indices of the suggested compounds, obtained using the ACD Labs 4.0 and NIST MS Search 2.0 soft-

Products of alkenylation of aromatic compounds with 1,3-pentadiene

Substrate	Conditions	Conversion, %	Content of products with indicated degree of alkenylation, mol %			
			mono-	di-	tri-	other
Phenol	Autoclave	88	57	31	–	–
	Reactor	96	45	51	Traces	–
p-Cresol	″	98	75	23	Traces	–
p-Nonylphenol*	Autoclave	74	51	23	–	–
α-Naphthol	″	80	47	33	–	–
	Reactor	100	32	68	–	–
Resorcinol	″	100	68	32	–	–
2-Methylresorcinol	Autoclave	70	53	17	Traces	–
	Reactor	100	15	85	–	–
Alkirez-1	″	100	46	54	–	–
α-Methylstyrene	″	100	58	–	–	42**

* Reaction duration 20 h.

** Compounds corresponding in composition to α-methylstyrene dimers.

ware.The reaction products were identified by gas chromatography–mass spectrometry (GC–MS) on a Shimadzu GCMS-QP 2010 quadrupole device.

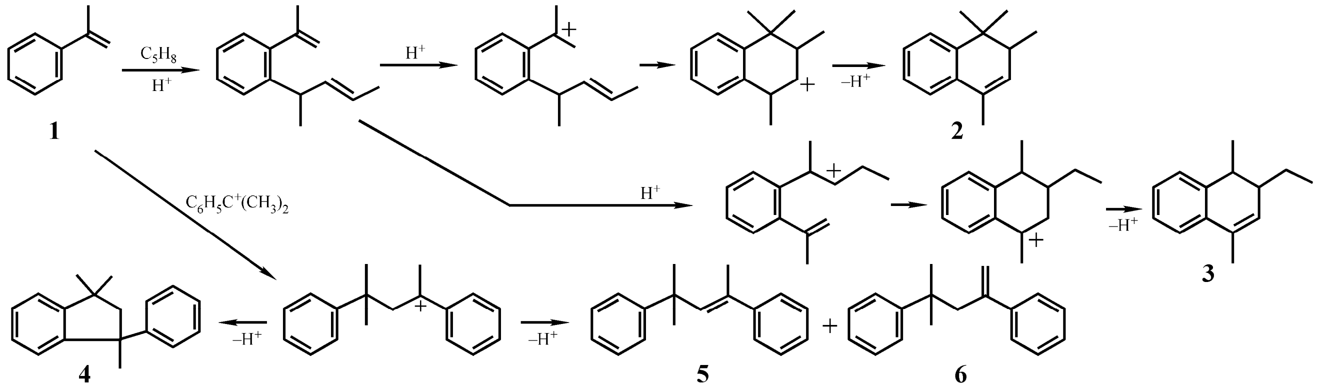
The quantitative composition of reaction mixtures was determined using a Kristall-2000M gas chromatograph equipped with a thermal conductivity detector. A 1-m steel column, 3 mm i.d., was packed with Chromaton N-AW-HMDS (0.25–0.315 mm) + 15% Apiezon L. The column was heated from 90 to 300°C at a rate of 16 deg min^{-1}. The flow rate of the carrier gas (He) was 20 cm^3 min^{-1}.

A TLC analysis was performed on Silufol UV-254 plates, using toluene as eluent. The component spots were developed with iodine vapor.

To convert the alkenylation products to the commercial form convenient for further use in rubber stock formulations, they were treated with hexamethylenetetramine. Transformation of the alkylate into the oligomeric form ("curing") was monitored by the dropping point measured by the ring-and-ball method according to GOST (State Standard) 11 506. The iodine number of the products was determined in accordance with GOST 17 823.2–72.

Data on the composition of reaction mixtures obtained by alkenylation of aromatic compounds with 1,3-pentadiene are listed in the table.

A GC–MS analysis showed that the reaction of α-methylstyrene **1** with 1,3-pentadiene yields four monoalkenylation products whose structure cannot be unambiguously determined from the mass spectra because of their similarity for the suggested isomers. However, the major product of a-methylstyrene monoalkenylation (>60% of the total amount) is, presumably, compound **2** (1,1,2,4-tetramethyl-1,2-dihydronaphthalene) or **3** (1,4-dimethyl-2-ethyl-1,2-dihydronaphthalene).



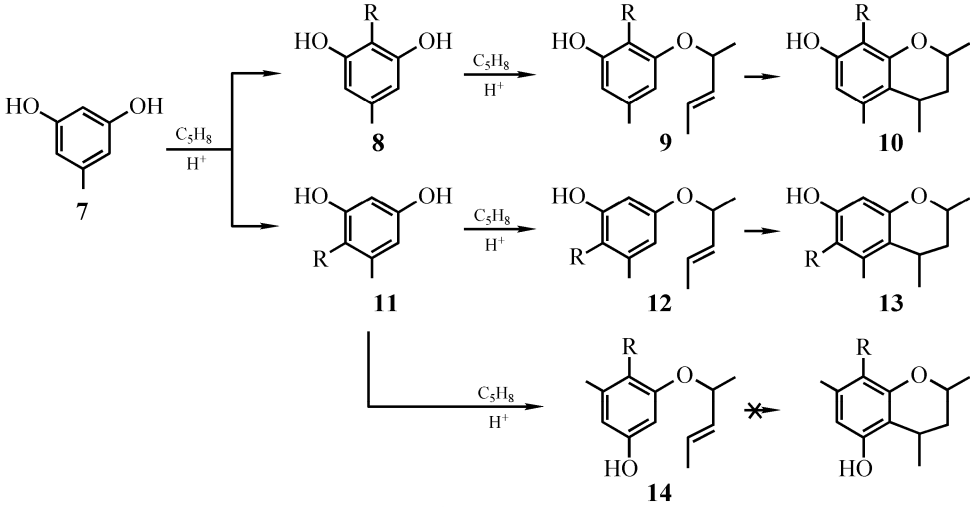
Scheme 1.

The reaction mixture obtained from α-methyl-styrene contains no dialkenylation products but contains dimers of the starting α-methylstyrene: 1,1,3-trimethyl-3-phenyl-2,3-dihydro-1*H*-indene **4**, (2-methyl-4-phen-ylpent-3-en-2-yl)benzene **5**, and (2-methyl-4-phenylpent-4-en-2-yl)benzene **6** in 75 : 10 : 15 molar ratio. This composiiton of the α-methylstyrene alken-ylation products agrees with the measured iodine nu-ber, 78.0 (value of 76.7, calculated on the assumption that the major monoalkenylkation products contain no more than one olefinic or cycloolefinic double bond in the molecule).

Transformations similar to those shown in Scheme 1 are also observed in alkenylation of styrene with piperylene.

A TLC analysis showed that the alkenylation of salicylic and benzoic acids with 1,3-pentadiene occurrs at the carboxy group and yields the corresponding pent-3-en-2-yl esters. With salicylic acid, the alkenylation also partially occurrs in the benzene ring owing to the activating effect of the phenolic hydroxyl.

Specifically the alkenylation of compounds containing phenolic hydroxy groups is of most interest from the standpoint of using the products as modifiers for polymer compounds. A detailed GC–MS analysis of the alkylate obtained from 5-methylresorcinol **7** allowed us to suggest the following scheme of its alkenylation with 1,3-pentadiene.



Scheme 2.

We found that the monoalkenylated fraction is composed of approximately equal amounts of 1,3-dihydroxy-5-methyl-2-(pent-3-en-2-yl)benzene **8** and 1,3-dihydroxy-5-methyl-4-(pent-3-en-2-yl)benzene **11**, formed by introduction of the alkenyl group into position 2 or 4 of the aromatic ring of 5-methylresorcinol, respectively. Further reaction of these monoalkenylation products with 1,3-pentadiene involves phenolic hydroxyls and yields mixed C,O-dialkenylation products: 5-methyl-2-(pent-3-en-2-yl)-3-(pent-3-en-2-yloxy)phenol **9**, 5-methyl-6-(pent-3-en-2-yl)-3-(pent-3-en-2-yloxy)phenol **12**, and 5-methyl-4-(pent-3-en-2-yl)-3-(pent-3-en-2-yloxy)phenol **14**, which are present in the reaction mixture in comparable amounts.

Under the reaction conditions, the dialkenylation products undergo partial cyclization. Compounds **9** and **12** form 2,4,5-trimethyl-8-(pent-3-en-2-yl)-3,4-dihydro-2*H*-benzo[*b*]pyran-7-ol 10 and 2,4,5-trimethyl-6-(pent-3-en-2-yl)-3,4-dihydro-2H-benzo[*b*]-pyran-7-ol **13**, respectively. Compounds **10** and **13** can be considered to be products of intramolecular electrophilic substitution in the aromatic ring with alkenyloxy groups as electrophilic agents. On the whole, the fraction of dialkenylated compounds contains about 70% C,O-dialkenylation products **9**, **12**, and **14**, with the remaining 30% being chroman derivatives **10** and **13**. It should be noted that we did not detect the expected cyclization product of compound **14** in the reaction mixture in noticeable amounts.

Bringing the alkylate obtained by the reaction of 1,3-pentadiene with 5-methylresorcinol or Alkirez-1 into the subsequent reaction with hexamethylenetetramine gives an oligomeric (so-called “cured”) product with a softening point of about 75°C. A special study showed that nearly the whole available amount of the monoalkenylated dihydric phenol **8** or **11** undergoes condensation to give Resorcinol–amino aldehyde resin, whereas dialkenylated compounds **9**, **10**, and **12–14** remain unchanged and control the melting point of the resulting oligomer. The cured product with a higher degree of oligomerization would have an unacceptably high melting point, which would make impossible its further use as a modifier of elastomeric compounds because of the insufficiently uniform distribution in the rubber stock.

The piperylene alkylate of Alkirez-1 condensed with hexamethylenetetramine (AP-U resin) was tested as modifier for improving the elastic-strength properties of thermoplastic elastomers (TPEs) of the composition SKEPT Elastokam 6305–PVD 10 803-020 (50:50 ratio), filled with BS-100 white black. The TPE modification with AP-U resin enhanced the strength (by up to 75%) and raised the relative elongation (by up to 20%) relative to the unmodified formulations.

The use of a silicic acid filler in the polymer compounds without addition of a phenolic modifier, as well as the modification without silicic acid filler, has nearly no effect on the TPE strength. The use of the reinforcing filler and oligomeric phenolic modifier in a combination affords a very significant improvement of the properties, i.e., a synergistic effect is observed.

Apparently, the alkenylresorcinol oligomer interacts, on the one hand, with the surface of BS-100 filler via phenolic hydroxyls and, on the other hand, with the rubber phase of TPE via alkenyl fragments, which strongly enhances the reinforcing effect of the filler [5].

In 2007, two batches of AP-U resin (25 kg) were produced on a pilot installation at the Central Plant Laboratory of the Kauchuk Joint-Stock Company (Sterli-tamak, Bashkortostan, Russia).

CONCLUSIONS

(1) Alkenylation of 5-methylresorcinol with 1,3-pentadiene yields complex mixtures of mono- and dialkenylated products. Monoalkenylation mainly occurs at the aromatic ring, whereas introduction of the second alkenyl group yields C,O-dialkenylated derivatives subsequently undergoing partial cyclization.

(2) Introduction of AP-U resin into polymer compounds based on thermoplastic elastomers is accompanied by a considerable enhancement of the strength characteristics of the ready items owing to the synergistic effect of interaction of the hydroxylcontaining moiety of the resin with the filler and of alkenyl substituents with the elastomer matrix.

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REFERENCES

1. Tutorskii, I.A., Potapov, E.E., and Shvarts, A.G., *Khimicheskaya modifikatsiya elastomerov* (Chemical Modification of Elastomers), Moscow: Khimiya, 1993.
2. Talantov, S.V. and Rossinskii, A.P., *Kauchuk Rezina*, 2000, no. 3, pp. 21–24.
3. Talantov, S.V., Rossinskii, A.P., and Derevkova, N.G., *Kauchuk Rezina*, 2001, no. 3, pp. 13–14.
4. Khitrin, S.V. and Alalykin, A.A., *Kauchuk Rezina*, 2001, no. 3, pp. 10–12.
5. Musin, I.N., Volkov, I.V., Kimel'blat, V.I., and Vol'fson, S.I., in *Kompozitsionnye materialy v aviastroenii i narodnom khozyaistve: Sbornik nauchykh trudov Vserossiiskoi nauchno-tekhnicheskoi konferentsii* (Composite Materials in Aircraft Building and National Economy: Proc. All-Russia Scientific and Technical Conf.), Kazan, October 5–8, 2000, pp. 35–40.