Photoreaction of polybutadiene in the presence of 1,3-diphenyl-1-butene, 1,2-dibromo-1,3-diphenylbutane, and 1,3-bis(4-nitrophenyl)-1-butene

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The influence of 1,3-diphenyl-1-butene, 1,2-dibromo-1,3-diphenylbutane, and 1,3-bis(4-nitrophenyl)-1-butene on the phototransformation reactions of polybutadiene in a thin film was studied. Qualitative differences in the effect of the substituents bonded to a molecule of the dimer of styrene were disclosed for bromo and nitro derivatives. The presence of 1,3-diphenyl-1-butene and its dibromo derivative produces an acceleration of the photooxidation reaction of polymer resulting in a reduction in length of the main chain in the solid phase. For 1,3-bis(4-nitrophenyl)-1-butene, a decreased rate of photooxidation reaction, prolongation of induction period, and decrease in the content of oxidation products is to be observed.

Изучалось влияние 1,3-дифенил-1-бутена, 1,2-дибром-1,3-дифенилбутана и 1,3-бис(4-нитрофенил)-1-бутена на реакции фотопревращения полибутадиена на тонких пленках. Были найдены качественные различия влияния заместителей на молекулу димера стирола с содержанием брома и нитрогруппы. Присутствие 1,3-дифенил-1-бутена и его дибромпроизводного вызывает ускорение фотоокислительной реакции полимера, приводящей в твердой фазе к понижению длины основной цепи. В случае 1,3-бис(4-нитрофенил)-1-бутена наблюдалось понижение скорости фотоокислительной реакции, продление периода индукции и понижение содержания продуктов окисления.

Abbreviations:

PBDPolybutadiene.DPB1,3-Diphenyl-1-butene.DPB-Br21,2-Dibromo-1,3-diphenylbutane.DPB-NO21,3-bis(4-Nitrophenyl)-1-butene.

The topic of this paper is a study of the interactions of some substituted oligomers of styrene which are able by the effect of ultraviolet radiation in polymer medium to crosslink linear chains or make change in their properties owing to photochemical grafting of macromolecules.

Experimental

1,3-Diphenyl-1-butene was prepared by dimerization of styrene in the presence of sulfuric acid [1]. The dibromo derivative was obtained by addition of bromine to DPB [2]. The dinitro derivative was prepared by nitration of DPB-Br₂ with fuming nitric acid in the medium of acetic acid [3] and subsequent elimination of bromine by means of KJ.

The substances were chromatographically purified in a column packed with neutral Al_2O_3 (activity according to Brockmann II) and finally three times recrystallized in methanol.

The progress of photochemical transformations in a system was investigated by means of infrared spectra (method of interrupted test) taken with a spectrometer Specord IR-71 (Zeiss, Jena) and by means of ultraviolet spectra (Specord UV VIS Zeiss, Jena).

The polymer films were prepared by casting a CCl₄ solution on NaCl plates. The polybutadiene rubber used for these investigations (JSR 021, Japan. Synt. Rubber Co.) was three times precipitated from a 2% solution in benzene into methanol in inert medium. The width of foils varied in the range $2.3 \times 10^{-2} - 2.5 \times 10^{-2}$ mm and was determined by means of absorbance $\bar{v}(C-H) = 1458$ cm⁻¹ [4]. The mean error was ± 0.006 and the maximum error was ± 0.012 . A high-pressure mercury discharge lamp HBO-500 (Narva BGW, Berlin, GDR) was applied to irradiation. The intensity of luminous flux of polychromate radiation was 2.03 J m⁻² s⁻¹. The exposed film was cooled by circulation of surrounding air. The temperature in the plane of impinging radiation varied in the range 23-24°C.

The gel portions of the irradiated films were pyrolized in an instrument C. Erba, Milan at 610° C with the purpose to find out whether DPB and its derivatives form crosslinks between vicinal chains. The time of duration of pyrolysis was 10 s. The flow rate of the carrier gas (nitrogen of electric bulb industry) was 40 cm³ min⁻¹. The pyrolyzer was connected with a gas chromatograph C. Erba 2300. The length of the chromatographic column was 2.5 m, its diameter being 2.3 mm. The nonpolar silicone elastomer E-301 (dimethylsilicone) separating according to boiling points was used as a stationary phase. Chromosorb W-80-10-Mesh served as a carrier. A flame ionization detector was used for detection. The gas chromatographic analysis was first performed isothermally at 50°C for 3 min and subsequently in the temperature 50–270°C according to the temperature programme 5°C/min. Samples of 1–2 mg were weighed for pyrolysis.

The boiling points of hydrocarbons were estimated by means of a calibrated scale for the mixture of n-alkanes and aromates expected in the products of pyrolysis. The accuracy of the boiling point estimation was $\pm 2^{\circ}$ C and depended on the time of duration of analysis. The boiling points of the found substances were estimated by injecting the standard hydrocarbons expected in the products of pyrolysis as described in literature [21].

Results and discussion

The photochemical transformations of linear polydienes are significantly affected by the presence of free oxygen [5]. Its presence in photolysis gives rise to peroxides and hydroperoxides which produce crosslinking in consecutive reactions. The degradation of polymer chain is a concomitant reaction. The infrared spectra of the irradiated polybutadiene in the absence and in the presence of DPB-NO₂ are represented in Fig. 1. Its results from the comparison of these spectra that remarkable changes appear in three regions by the effect of ultraviolet irradiation of PBD, *i.e.* 750—1450 cm⁻¹, 1670—1770 cm⁻¹, and 3450 cm⁻¹. The characterization of the absorption bands in the region 750—1450 cm⁻¹ has not yet been satisfactorily carried out. In general, an increase in absorption with time of photooxidation is to be observed in this region, which is consistent with the results obtained by *Beavan et al.* [6—9].

The character of the observed changes in infrared spectra was not affected by the derivatives of DPB. It ensues from Figs. 2 and 3 that the presence of the added substances has influence on the length of induction period, rate of photooxidation, and concentration of photooxidation products. The distinct induction period observed with pure polybutadiene decreases to half of its value by an addition of DPB and vanishes completely in the presence of DPB-Br₂. In the last case, the C—Br bond is likely the first to split and give free radicals which compete in a radical oxidation reaction on polymer chain. Further course of reaction may be described by the mechanism generally accepted for oxidation of organic compounds [10]. A decrease in the apparent temporal retardation of the process by the presence of DPB may be explained by increased absorption of light radiation owing to the presence of aromatic chromophore.



Fig. 1. Infrared spectrum of destroyed polybutadiene.
 Nonirradiated polymer; - - - polymer irradiated for 475 min; polymer containing 2.5 wt % of DPB-NO₂ and irradiated for 500 min.

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Provided DPB-NO₂ is present in the exposed film of polybutadiene, a prolongation of induction period and decrease in concentration of oxidation products is to be observed. A decrease in the rate of oxidation is thus obvious. A loss of nitro groups in the process of photooxidation (Fig. 4) may be in this case due to an indirect splitting of the C_{ar} —NO₂ bond in the system of consecutive reactions. In conformity with some results obtained by the study of photolysis of the aromatic carbonyl compounds [11, 12], we assume in the first stage of the investigated reaction a formation of carbonyl intermediates which react like *o*-nitrobenzal-



Fig. 4. Variation of absorbance with time at the wavenumbers 1345 cm^{-1} (1) and 1350 cm^{-1} (2) in the infrared spectrum of polybutadiene film containing 4.5 wt % of DPB-NO₂.

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dehyde to give rise to an azoxy group. This group undergoes further oxidation to yield an azo product prone to splitting. Thus the resulting product of the mentioned sequence of consecutive reactions is a biradical with good stability and defect in the aromatic ring in the *para* position with respect to the fundamental butene chain. This idea is also confirmed by the formation of bright red colour. The experimental confirmation of this assumption is the topic of our subsequent study [13] in which we have evidenced that the photolysis of the nitro derivative in 2-propyl alcohol in the presence of oxygen gives 1,3-diphenyl-1-butene.

A comparison of Fig. 2 and Fig. 3 shows an evident parallel in the temporal change in absorbance at 3450 and 1720 cm⁻¹. The pertinent bands are attributed to the hydroxyl groups (3450 cm^{-1}) and the saturated ketones (1720 cm^{-1}) which may be expected in the spots of structural vinyl defects [5].

For the β splitting of alkoxide radicals we may write

In the beginning of these investigations we were guided by the assumption that, in analogy to anthracene [14], the cyclic peroxides derived from 1,3-diphenyl-1-butene and its derivatives could arise in the matrix of polybutadiene rubber by the effect of ultraviolet radiation. In order to prove their formation, the thoroughly degassed crosslinked portions of samples which had previously been deprived of soluble parts by careful benzene extraction were subjected to pyrolysis. The chromatograms of the pyrolysis products (Table 1) obtained in the absence and in the presence of the substituted oligomers of styrene evidently show a qualitative difference. In each case, a variable content of splitting products of the hydrocarbon fraction C_1-C_6 is to be observed. The first distinct

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Table 1 Pyrolysis of gel fractions of polybutadiene rubber $t_{ir} = 300$ min, $c_x = 2.5$ wt % of polymer tention Boiling point Content in wt % of product

No.	Retention time ^e	Boiling point of product – °C	Content in wt %				
			PBD	DPB	DPB-Br ₂	DPB-NO ₂	
1	0.42	$C_1, C_2 C_3^{b}$	18.83	7.125	29.21	3.86	
2	0.42-0.52	C ^b	12.93	36.09	41.205	39.36	
3	0.52-0.68	C ^b ₅	11.15	5.11	3.21	4.78	
4	0.68-0.94	C6	11.12	1.26		1.41	
5	1.79	115	2.19	9.77	9.275	17.97	
6	3.39	191	2.87	18.705		0.35	
7	3.93	219	1.08	0.58	_	1.61	
		(Naphthalene)		*			
8	4.23	231	1.556	15.12	2.21	_	

a) Rel. u. with respect to benzene.

b) Expected hydrocarbons.

peak which characterizes the differences in pyrolysis products corresponds to the hydrocarbon with the boiling point 115° C. As evident from Table 1, an addition of DPB raises the content of this hydrocarbon to the fourfold while an addition of DPB-NO₂ raises it to the eightfold. With respect to the boiling point, a structure of the type of cyclohexadienes, cyclohexenes, methylcyclohexene or cycloheptene may be attributed to this portion. As stated by *Golub* and *Stephens* [15—17], the formation of cyclic portions is characteristic of the photolysis of poly-1,2-butadiene by the effect of ultraviolet radiation. In our case, the presence of unsaturated alkanes may by thus ascribed to defects of the type

present in poly-1,4-butadiene. The results of the study of photoisomerization of 1,6-heptadiene in the gaseous phase to four-, five-, and six-membered cyclanes [18, 19] may serve as a good precedent for that statement.

The second peak which significantly characterizes the differences in pyrolysis products corresponds to a hydrocarbon with the boiling point 191°C. An addition of DPB into polybutadiene raises its content approximately to the eightfold. However, it does not appear at all in the presence of the brominated dimer and its content is very low in the presence of the nitro derivative. A structure of the type of

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indene or indane is to be attributed to this hydrocarbon and its formation must be connected with the splitting off of DPB from the side chain and its subsequent thermal isomerization to *cis*-, *trans*-1-methyl-3-phenylindane [20]. The splitting of DPB is also responsible for the formation of a hydrocarbon with the boiling point 231° C.

As pointed out by authors [21], different aromatic hydrocarbons also arise in slight concentrations, especially from the *cis* isomer of the basic segment, in thermal destruction of polybutadiene.

In general, it may be stated that the pyrolysis of the crosslinked portions of polybutadiene containing DPB-NO₂ gives rise to a great number of various products — hydrocarbons, oxygenous compounds, and nitro derivatives. The presence of aromatic portions in the products of pyrolysis does not refute the primary idea according to which cyclic peroxides of the type



arising by photooxidation of nitro dimer (DPB-NO₂) are able to initiate crosslinking of the linear macromolecules of polybutadiene.

On the basis of these results, it may be stated that the presence of the substituted oligomer styrenes significantly affects the photooxidation reactions in a polybutadiene film. As for DPB and its brominated derivative, it may be assumed that these substances function mainly as catalysts of the photooxidation reaction. In this case, the formation of a portion of pyrolysis products consisting of higher hydrocarbons can be explained by cyclization of polymer chain though a grafting of dimer on linear chains should not be fully ruled out. The crosslinking reaction prevails in the presence of DPB-NO₂ and the crosslinks are formed by residual DPB or oxygen bridges. For the time being, this hypothesis is also confirmed by the results of the pyrolysis of gel portion. The products of this pyrolysis contain considerable amounts of hydrocarbons derived from benzene.

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