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Summary

Poly(2,3-dimethylbutadiene-1,3) containing *cis*-1,4, *trans*-1,4, and 1,2 structural units in various proportions undergoes rapid oxidation even at room temperature. The process of oxidation is accompanied by cyclization. The concentration of peroxides that form at room temperature is relatively very high, reaching the value of one peroxidic group per 16 monomeric units. The formation of six-membered rings involving the peroxidic bonds in poly(2,3-dimethylbutadiene) is accompanied by degradation.

It has been observed that linear poly(2,3-dimethylbutadiene-1,3) with predominantly 1,4 structural units is readily oxidized by air oxygen even at room temperature (*1,2*). In this study the course of oxidation of poly(2,3-dimethylbutadiene-1,3) has been studied.

EXPERIMENTAL

Synthesis of Poly(2,3-dimethylbutadiene-1,3)

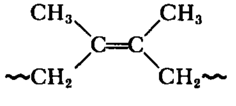
Sample BS-16. Twenty milliliters of 2,3-dimethylbutadiene-1,3, dried by distillation over sodium hydride, was injected by means of a hypodermic syringe into a solution of the Al(iso-$C_4H_9)_2Cl$ + $CoCl_2$·py catalyst in 50 ml of benzene. The molar ratio of the aluminum component to the pyridine complex of cobaltous chloride was 900:1. The amount of the cobalt component was 0.005 mmole. The reaction was carried out in a nitrogen atmosphere at 20°C. After a 48-hr reaction period the polymer was isolated by precipitation with methanol. The polymer, obtained in a yield of 1.2 g, contained 48% *cis*-1,4, 32% *trans*-1,4, and 19% of 1,2 units, according to IR analysis, using absorption bands at 1200, 1155, and 890 cm^{-1}, respectively, and relatively pure *cis*-1,4 and *trans*-1,4-poly(2,3-dimethylbutadiene) and 3,4-polyisoprene as standards.

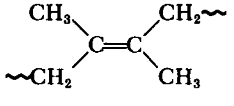
Sample BS-17. This polymer was prepared in an all-glass apparatus in the absence of an inert gas. The polymerization catalyst was a Ziegler-type system from 0.9 mmole of $Al(iso\text{-}C_4H_9)_3$ and 0.25 mmole of $TiCl_4$. Glass ampules containing *n*-heptane solutions of the catalyst components were placed into the polymerization apparatus, the system was carefully evacuated, then 40 ml of dried *n*-heptane was condensed from the reservoir into the cooled reaction vessel. The ampules with the catalyst constituents were broken and the catalyst was allowed to "age" for 20 min at 20°C. The system was then cooled again and 5 ml of the monomer was condensed from the reservoir into the polymerization vessel. The temperature was again adjusted to 20°C. The yield after 20 hr was 1.6 g of a white, sticky powder of polydimethylbutadiene with predominantly *cis*-1,4 structure (80%), 20% of *trans*-1,4, and less than 1% of 1,2 units.

Sample BS-20. Fifteen milliliters of freshly distilled 2,3-dimethylbutadiene-1,3 was introduced in a stream of nitrogen into a catalyst system containing the reaction product of 2.7 mmoles of $Al(iso\text{-}C_4H_9)_3$ and 0.7 mmole of $TiCl_4$ in 50 ml of benzene dried over NaH. The order of mixing the components was as follows: benzene, $TiCl_4$, $Al(iso\text{-}C_4H_9)_3$, monomer. The catalyst was allowed to "age" for 20 min before the monomer was added. The reaction temperature was 20°C. The yield of the polymer after 24 hr was 1.1 g. The polymer structure was 17% of *cis*-1,4, 49% of *trans*-1,4, less than 0.1% of 1,2 units and cyclic structure.

All samples were precipitated several times.

Oxidation. Samples of poly(2,3-dimethylbutadiene-1,3) (DMB) with various contents of *cis*-1,4 (A), *trans*-1,4 (B), and 1,2 (C) units,


(A)


(B)

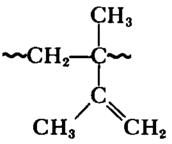

(C)

TABLE 1

Polymer	Oxidation		Band intensity of group[a]				Concn. of —O—O—[b]	Mol. wt.[c]	$C=C$, %[d]
	Temp., °C	Time, hr	$C=O$, A(1720) × 10^3 or A(1740) × 10^3	CH_3, A(1380) × 10^3	$C(CH_3)=CH_2$, A(890) × 10^3	$C(CH_3)=CH-$, A(852) × 10^3			
DMB[e]	30	0	031	538		0	125	1210	70
		0.45					42	1380	20
Sample		0.66					31	1340	
BS-20		1.0	060	562			23	1320	18.5
		1.3					16	1070	
		1.6					24	1170	21
		2.25	130	581					
		3.3	139	593					
		5.0	182	621					
		6.0	194	625		060			
		6.6	236	630					
		8.0	265	627					
		9.5	287	650					
		11.0	307	666					
		13.0	332	667					
		23.0	397	693		114			
		29.0	440	702					
DMB	20	0	013	260	243	010			
		72	114	278	157	041			
Sample		260	263	319	070	068			
BS-16[f]		286	237	309	074	074			
		308	244	300	071	071			
		402	299	361	079	087			
		428	280	345	070	083			
DMB	20	0	010	202	010	013			
		27	006	198	010	011			
Sample		124	036	228	011	017			
BS-17[f]		146	059	258	010	024			
		172	072	230	010	028			
		219	100	259	016	041			
		239	134	269	014	044			
		291	134	274	015	048			
		338	154	277	019	056			
		460	180	295	019	059			
		532	191	294	021	066			

[a] Infrared spectrum in KBr, base-line method, A(1380) = absorbance at 1380 cm^{-1}.

[b] Number of monomer units for one peroxide group.

[c] See experimental part.

[d] ICl method.

[e] DMB, poly(2,3-dimethylbutadiene-1,3).

[f] Sample oxidized as powder.

are oxidized by air oxygen even at room temperature. Therefore the polymers were dissolved in benzene immediately after their preparation and the solutions were stored at dry-ice temperature. In oxidation studies, the polymers were deposited as thin films on glass plates (about 0.03 mm thick) and on plates of potassium bromide. The films were subjected to the action of air oxygen at room or elevated temperatures (Table 1). In some cases the polymer was oxidized in the form of powder. The variations in the contents of specific functional groups were checked by infrared spectroscopy. The specimens designed for the analysis of peroxides and the determination of molecular weight were withdrawn from the film deposited on the glass plate.

Infrared Examination. The infrared spectra were recorded in the range 400–3800 cm^{-1}. Changes of the concentration of the $>C{=}O$ groups were measured quantitatively from absorption peaks at 1720 cm^{-1}. The effect of stray light was eliminated by determination of the values of $A(1720) = \log[I(1900)/I(1720)]$. The base-line method was used in the determination of the CH_3 groups (1380 cm^{-1}), $-C(CH_3){=}CH_2$ groups (890 cm^{-1}), and $-C(CH_3){=}CH$ groups (850 cm^{-1}).

Determination of Peroxides. The content of peroxides in the oxidized polymers was determined by the method based on oxidation of the leucobase of methylene blue (*3*) in the manner described by Novák and Mika (*4*).

Determination of Molecular Weights. Molecular weights of the oxidized polymers were determined by the thermometric distillation method at a concentration of about 1%. Calibration was set to squalane (MW = 423).

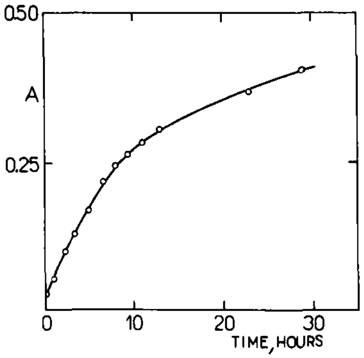


FIG. 1. Oxidation of poly(2,3-dimethylbutadiene-1,3) checked by absorbance of the absorption band of $C{=}O$ groups (sample BS-20, see Table 1).

Determination of Double Bonds. For the determination of double bonds the iodine monochloride method was used.

RESULTS

Table 1 presents the results of the experiments. The changes of the content of the $>\!C{=}O$ groups, as determined from the absorption intensities at 1720 cm^{-1} as a function of the time of the experiment, are shown in Fig. 1. The entire oxidation run was made on one film of the polymer.

DISCUSSION

The commonly accepted mechanism of oxidation of hydrocarbon polymers assumes the formation of a primary macroradical R· and the following consecutive reactions (5):

$$R\cdot + O_2 \rightarrow ROO\cdot \qquad (1)$$

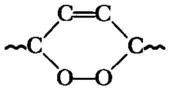
$$ROO\cdot + RH \rightarrow ROOH + R\cdot \qquad (2)$$

The hydroperoxide radical splits to two radicals, which is a cause of branching of the chain reaction. The consecutive reactions lead to the formation of the $>\!C{=}O$ groups and diminishing of the content of the $>\!C{=}C\!<$ groups. Mutual coupling of the macroradicals causes cross-linking of the oxidized polymers and the loss of solubility. The radicals form preferentially at the α position to the double bond.

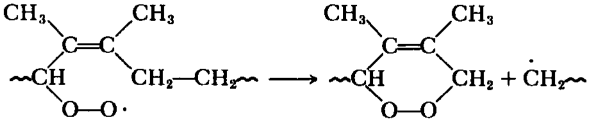
The easier oxidizability of *cis*-1,4-polyisoprene compared to *cis*-1,4-polybutadiene indicates that the radical $-\dot{C}H-C(CH_3)=CH-CH_2-$ forms more easily than the radical $-\dot{C}H-CH=CH-CH_2-$ (or the former radical is more reactive toward molecular oxygen than the latter). The higher rate of oxidation of poly(2,3-dimethylbutadiene-1,3) (Fig. 1 and Table 1) can be explained by the presence of twice as many $-CH_2-C(CH_3)=$ groups in DMB as in polyisoprene.

The oxidation curve (Fig. 1) is not of the characteristic S-shape form which is known in the case of most polydienes. Since the samples were isolated and washed in the same manner as the synthetic polyisoprenes obtained with the aid of similar polymerization catalysts, we assume that the enormous oxidizability of polydimethylbutadiene is not caused by the catalytic action of residual cobalt or titanium. The difference between polydimethylbutadiene and synthetic polyisoprene which contains titanium residues is incomparably higher than the difference between that polyisoprene and natural deproteinized Hevea (8). Of course, the influence of residual metals cannot be neglected.

The explanation for the very high rate of oxidation and of the unusual shape of the oxidation curve probably lies in different mechanisms for the oxidation which follows from the structures of the peroxides. In the diene polymers, reaction (2) leads to the formation of hydroperoxides ROOH and the consecutive reaction to the formation of peroxides ROOR (6,7). In addition to these reactions we can assume the formation of cyclic peroxides with four, five, six, or more members in the ring.



The closure of a six-membered ring is favored in poly(2,3-dimethylbutadiene-1,3), which has two —$CH_2C(CH_3)=$ groups with reactive hydrogen. However, we assume that in the case of DMB this reaction is accompanied by degradation of the main polymer chain:



(3)

The new methylene free radical abstracts hydrogen from another molecule and gives a new CH_3 group. An increase in the concentration of the terminal CH_3 groups was readily observed from an increase in the intensity of the 1380-cm^{-1} band (Table 1). The absorption band at 1460 cm^{-1}, which is composed of CH_2 and CH_3 vibrations, remains practically unchanged because the decrease of the concentration of CH_2 groups is compensated by the increase of CH_3 groups.

No increase of concentration of the CH_3 groups was observed during the oxidation of *cis*-1,4-polyisoprene (8). This is in agree-

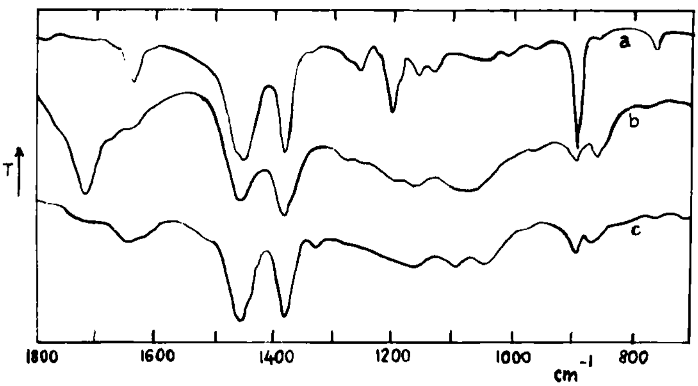


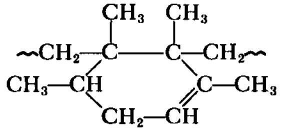
FIG. 2. Infrared spectrum of (a) poly(2,3-dimethylbutadiene-1,3) with 20% of 1,2 units; (b) the same polymer after oxidation for 428 hr at 20°C; (c) cyclized polymer obtained by radical polymerization (*1*).

ment with our proposal, since the occurrence of reaction (3) in polyisoprene is rare.

On the other hand, the decrease of molecular weight which would prove this mechanism has not been observed. The decrease of molecular weight caused by oxidation is most probably compensated by cross-linking of the macromolecules, which in the later stages results in the loss of solubility.

The formation of six-membered rings in DMB is also favored by the deformation of the valence angles caused by two methyl groups at a double bond in *cis* configuration.

The appearance and a marked increase of intensity of the absorption band at 852 cm^{-1} (Fig. 2), which was assigned to the out-of plane C—H deformation vibration in the —C(CH_3)═CH— group, indicates another reaction proceeding simultaneously during oxidation of DMB. At the same time, the concentration of C═C double bonds decreases. We propose that cyclization occurs as a side reaction with the formation of the following units (*1*):



which includes the indicated atom groups. The striking similarity of the infrared absorption spectrum of the oxidized polymer to the spectrum of cyclized polymer, with the exception of the bands of oxidation products at 1720 cm^{-1} and a total increase of absorption between 1200 cm^{-1} and 1000 cm^{-1}, shows that cyclization must be considered in the oxidation reaction.

Also, the decrease of the content of vinylidene groups of 1,2-polydimethylbutadiene units at 890 cm^{-1} is not necessarily caused by oxidation of these groups. It may be caused by cyclization, which occurs even at room temperature, as has been observed in the case of 3,4-polyisoprene (*8*).

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Zusammenfassung

Poly(2,3-dimethylbutadien-1,3), das sowohl *cis*-1,4, *trans*-1,4, und -1,2 Bausteine in verschiedenen Mengen enthält, unterliegt einer raschen Oxydation sogar schon bei gewöhnlicher Temperatur. Der Oxydationsprozess ist von Ringbildung begleitet. Die Konzentration der Peroxyde, die sich bei gewöhnlicher Temperatur bilden, ist verhältnismässig sehr hoch, sie erreicht den Wert einer Peroxydgruppe für 16 monomere Einheiten. Die Bildung von sechsgliederigen Ringen unter Einbeziehung der peroxydischen Bindungen von Poly(2,3-dimethylbutadien) erfolgt unter Zersetzung.

Résumé

Le poly(2,3-dimethylbutadiene-1,3) qui contien d'unités *cis*-1,4, *trans*-1,4, et 1,2 en proportion varieé subi oxydation rapide quand meme la tempéra-

ture est ordinaire. Le procès d'oxydation est accompagné de cyclisation. Le concentration des peroxydes qui se forment a température ordinaire est relativement très elevé et atteind des valeurs d'un group de peroxyde pour 16 unités monomerique. La formation d'unités cyclique de six membres avec les liasons peroxydiques en poly(2,3-dimethylbutadiene) est accompagné par dégradation.

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