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Introduction of cyclooctadienyl substituents into 1,4-polybutadiene

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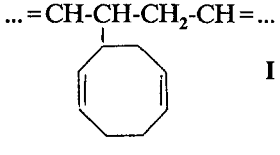
Summary

1,4-Polybutadiene was modified by reaction with 1,5-cyclooctadiene and dicumyl peroxide as radical donor. Evidence of modification was provided by metathesis degradation with (E)-4-octene using the catalyst $WCl_6/Sn(CH_3)_4$. The low-molecular-weight products were identified by combination of gas chromatography (GC) and mass spectrometry (MS). Products characteristic of polybutadiene with cyclooctadienyl substituents at the methylene groups were found. Substitution was partially coupled with double bond shift. The structure of the modified polymer corresponds to polybutadiene crosslinked by dehydrodimerization of methylene groups.

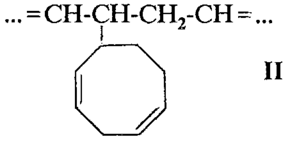
Introduction

In previous work we have introduced aralkyl substituents into unsaturated polymers by radical reactions with alkylbenzenes (e.g. toluene), using dicumyl peroxide as radical donor (1). The radicals formed in a thermolysis of the peroxide abstract hydrogen from the solvent and the polymer. A combination of the solvent radicals with the polymer radicals follows. This aralkylation is coupled with partial double bond shift (allyl rearrangement).

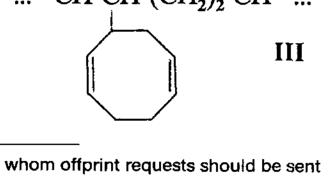
The present investigation deals with the introduction of cyclooctadienyl substituents into 1,4-polybutadiene by reaction with 1,5-cyclooctadiene and dicumyl peroxide. The crosslinking of the 1,4-polybutadiene with radicals from the peroxide, which is also possible, is prevented by using a large excess of the cyclooctadiene. According to other dehydrodimerization reactions (2), the structures **I** to **IV** (considered from one double bond of the polymer chain to the next) can be expected in the substituted polymer.



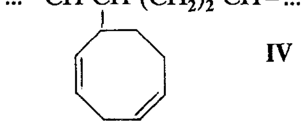
I



II



III



IV

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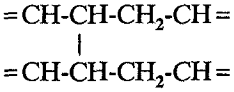
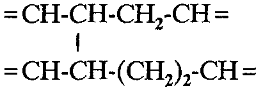
Spectroscopic evidence of the cyclooctadienyl substituents proved difficult, if not impossible, because polymer and substituents are chemically identical. Both starting materials (1,4-polybutadiene and 1,5-cyclooctadiene) consist of butanediylidene units.

The structures in the substituted polymer were therefore investigated via degradation by olefin metathesis with (E)-4-octene (3). The units **A** (from **I**), **B** (from **II** or **III**) and **C** (from **IV**) remain after metathesis cleavage of the double bonds in the cyclooctadienyl substituents. The metathesis products can also contain butanediylidene units **D** of 1,4-polybutadiene (or 2,6-cyclooctadienyl substituents) and propanediylidene units **E**, formed by double bond shift during the substitution reaction. Alkylidene groups which do not form cycles combine with butylidene residues **F** of 4-octene.



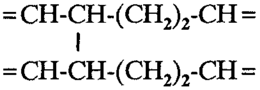
$$\begin{array}{l}=CH\text{-}CH\text{-}CH_2\text{-}CH= \\ \quad\;\;\;| \\ =CH\text{-}CH\text{-}CH_2\text{-}CH=\end{array}$$

A



$$\begin{array}{l}=CH\text{-}CH\text{-}CH_2\text{-}CH= \\ \quad\;\;\;| \\ =CH\text{-}CH\text{-}(CH_2)_2\text{-}CH=\end{array}$$

B



$$\begin{array}{l}=CH\text{-}CH\text{-}(CH_2)_2\text{-}CH= \\ \quad\;\;\;| \\ =CH\text{-}CH\text{-}(CH_2)_2\text{-}CH=\end{array}$$

C

$=CH\text{-}CH_2\text{-}CH_2\text{-}CH=$ **D**

$=CH\text{-}CH_2\text{-}CH=$ **E**

$=CH\text{-}(CH_2)_2\text{-}CH_3$ **F**

Experimental

0.50 g (9.3 mmol with respect to monomer units) of cis-1,4-polybutadiene (Buna CB 11$^{(R)}$, Hüls AG, ca. 95% cis-1,4 addition) were dissolved in 20 ml (163 mmol) of 1,5-cyclooctadiene under nitrogen. 2.0 g (7.4 mmol) of dicumyl peroxide were added and the reaction mixture was heated to 130 °C. Further portions of 2.0 g of dicumyl peroxide were added after 12 and 24 h. After a total reaction time of 48 h, the reaction mixture was cooled and the polymer precipitated with 100 ml of methanol. For purification, the polymer was reprecipitated with toluene/methanol and dried under vacuum. The IR spectrum was similar to that of 1,4-polybutadiene but showed cis-trans isomerization and loss of double bonds.

Metathesis degradation was carried out under nitrogen as described previously (3). 50 mg of modified 1,4-polybutadiene were dissolved in 1.5 ml of chlorobenzene at 40 °C. 1.0 ml of (E)-4-octene, 1.0 ml of a 0.2 molar solution of $Sn(CH_3)_4$ in chlorobenzene and 1.0 ml of a 0.1 molar solution of WCl_6 in chlorobenzene were added. The reaction mixture was stirred for 20 h at 60 °C. The catalyst was then destroyed with methanol and the liquid mixture was concentrated.

GC/MS analysis was performed with a combination GC Varian 3700 (25 m capillary column HP 1, 100% methylsilicone) / MS Finnigan-MAT 212 (electron impact ionization at 120 eV); injector temperature 280 °C; temperature program: 5 min at 60 °C, heating rate 10 °C/min, final temperature 280 °C.

Results and discussion

A section of the gas chromatogram of a concentrated degradation mixture is shown in Fig. 1. 4,7-Undecadiene (**1**) contains units **E** + 2 **F** and 4,8-dodecadiene (**2**) units **D** + 2 **F**. The degradation products of polybutadiene (1,4- or 1,2-linked) are well-known (4) and will not be discussed again here. The products **3** to **8** are attributable to crosslinks **A** to **C**.

$C_3H_7\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}C_3H_7$ **1**

$C_3H_7\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH\text{-}C_3H_7$ **2**

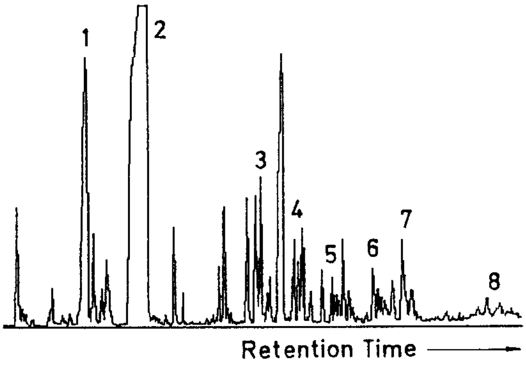


Fig. 1. Metathesis degradation of a 1,4-polybutadiene with cycloocadienyl substituents in the presence of (4)-octene, gas chromatogram of the reaction mixture:
1 = 4,7-undecadiene,
2 = 4,8-dodecadiene,
3 = $C_{16}H_{26}$, **4** = $C_{17}H_{28}$,
5 = $C_{18}H_{30}$, **6** = $C_{20}H_{32}$,
7 = $C_{21}H_{34}$, **8** = $C_{24}H_{42}$

Tab. 1 gives the empirical formulas of products **3** to **8** (deduced from the molecule ions M^+ in MS), the units and the number of possible structural isomers with 5- to 8-membered rings.

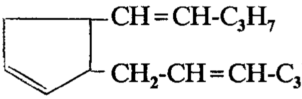
Tab. 1. Possible structural isomers of degradation products

product group	formula	units	number of isomers with n-membered rings n = 5	6	7	8	sum of isomers
3	$C_{16}H_{26}$	**A** + 2**F**	1	1	-	-	2
4	$C_{17}H_{28}$	**B** + 2**F**	2	1	1	-	4
5	$C_{18}H_{30}$	**C** + 2**F**	1	1	-	1	3
6	$C_{20}H_{32}$	**A** + **D** + 2**F**	2	1	-	-	13
		B + **E** + 2**F**	4	2	2	-	
		I + 2**F**	-	-	-	1	
		II + 2**F**	-	-	-	1	
7	$C_{21}H_{34}$	**B** + **D** + 2**F**	4	2	2	-	15
		C + **E** + 2**F**	2	2	-	1	
		III + 2**F**	-	-	-	1	
		IV + 2**F**	-	-	-	1	
8	$C_{24}H_{42}$	**A** + 4**F**	-	-	-	-	1

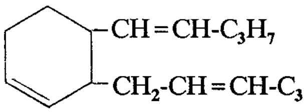
Only rings with one double bond are considered as metathesis products in Tab. 1, because the formation of small rings with more than one alkanediylidene group has a very low probability in the given conditions; for example, 1,5-cyclooctadiene was not found in metathesis degradation of 1,4-polybutadiene. But products with unchanged cyclooctadienyl rings of the parent substituted polybutadiene are possible.

For the structural investigation of the polymer it is not always necessary to know which special isomeric degradation product is formed. The formation of products in olefin metathesis is not only determined by thermodynamics but also kinetically. Thus different structural isomers or stereoiosomers may be obtained, dependent on the stage of the reaction, and the mass spectrum may be attributable to more than one isomer if the separation in GC is incomplete.

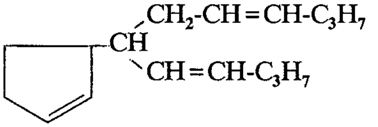
A decision between two structural isomers has to be made in the case of products **3** (M^+ = 218), see Fig. 2. The fragmentation in the mass spectrum points to 3-(2-hexenyl)-4-(1-pentenyl)cyclopentene (**3a**). Four isomers are possible in the case of product **4** (M^+ = 232), see Fig. 3. 3-(2-hexenyl)-4-(1-pentenyl)-cyclohexene (**4a**) or 6-(2-cyclopentenyl)-4,8-dodecadiene (**4b**) are the most probable. In the case of product **5** (M^+ = 246), see Fig. 4, there are three possible structures. The fragmentation points to the cyclohexene derivative **5a**. Products **6** (m/z = 272 (M^+), 228, 214, 189, 147, 133, 119) and **7** (m/z = 286 (M^+), 243, 219, 203, 163, 149, 135, 119) proved difficult to identify because of the large number of isomers expected. Product **8** is 7,8-bis(1-pentenyl)-4,10-tetradecadiene (m/z = 330 (M^+), 285, 271, 260, 245, 229).



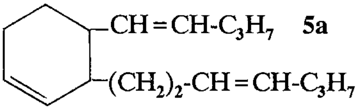
3a



4a



4b



5a

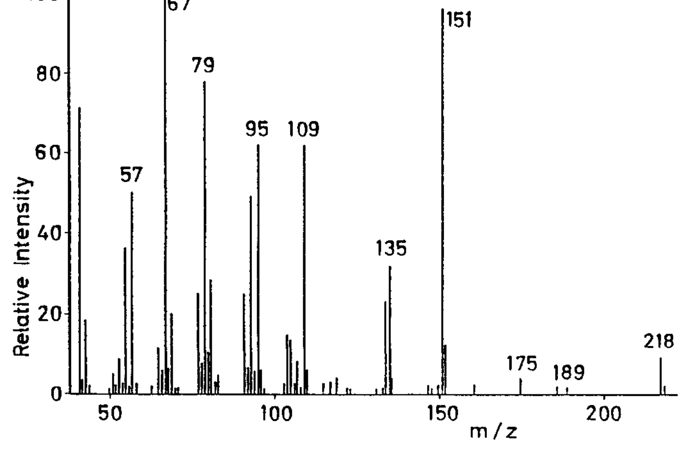


Fig. 2. Metathesis degradation of a 1,4-polybutadiene with cyclooctadienyl substituents in the presence of (4)-octene, mass spectrum of product $C_{16}H_{26}$ (3)

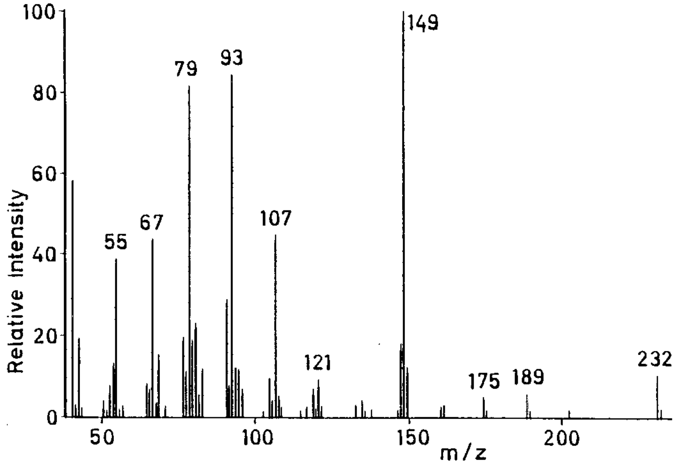


Fig. 3. Metathesis degradation of a 1,4-polybutadiene with cyclooctadienyl substituents in the presence of (4)-octene, mass spectrum of product $C_{17}H_{28}$ (4)

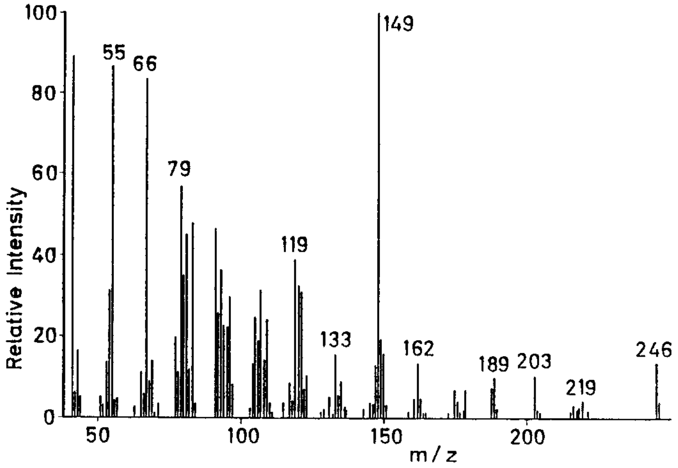
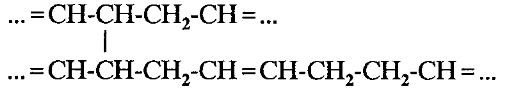


Fig. 4. Metathesis degradation of a 1,4-polybutadiene with cyclooctadienyl substituents in the presence of (4)-octene, mass spectrum of product $C_{18}H_{30}$ (5)

Polybutadiene with cyclooctadienyl substituents deserves attention as a model compound of a polybutadiene crosslinked by reaction of the methylene groups. For example, structure **I** in polybutadiene with cyclooctadienyl substituents corresponds to **V** in crosslinked polybutadiene.



$$\begin{array}{l} ...=CH\text{-}CH\text{-}CH_2\text{-}CH=... \\ \phantom{...=CH\text{-}}| \\ ...=CH\text{-}CH\text{-}CH_2\text{-}CH=CH\text{-}CH_2\text{-}CH_2\text{-}CH=... \end{array}$$

V

It should be remembered that the structure of 1,4-polybutadiene crosslinked via radical mechanisms is still open to discussion. Many observations support the assumption that the radical crosslinking of 1,4-polybutadiene in the absence of a solvent leads preferably to an oligomerization and cyclization of the double bonds (5-8) in connection with hydrogen abstraction from the methylene groups and dehydrodimerization (9). Simple CH-CH crosslinks with units **A** to **C** are formed in solution under certain reaction conditions (10). Computer simulation has shown that even in this case rather complicated networks result.

Being soluble, polybutadiene with cyclooctadienyl substituents could with advantage be used for comparison in the chemical investigation of the insoluble crosslinked polybutadiene.

Acknowledgements

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