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DEGRADATION OF UNSATURATED POLYMERS BY OLEFIN METATHESIS

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ABSTRACT

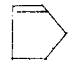
Degradation of unsaturated polymers by olefin metathesis ("MUP degradation") followed by identification of the low-molecular-weight degradation products with a combination of gas chromatography (GC) and mass spectrometry (MS) is a valuable method for structure investigation. The examples discussed here are the investigation of butadiene copolymers containing silicon in the comonomer and of products obtained by subsequent modification or crosslinking of poly(butadiene-*alt*-propene). MUP degradation is also useful for the determination of fillers in a crosslinked polymer matrix. The degradation to soluble polymers is sufficient here. The example under consideration is determination of carbon black in vulcanizates of natural rubber.

1. INTRODUCTION

1.1. General

Olefin metathesis is a catalytic scission of $-CH=CH-$ double bonds followed by a recombination; the intermediates are carbenes [1, 2]. In principle, the resulting product distributions can be calculated by computer simulation (Monte Carlo calculation) [3].

Degradation of polymers with $-CH=CH-$ double bonds in the backbone via olefin metathesis is interesting as a future possibility of recycling of wastes of polyalkenylenes (polyalkenamers). An example of a suitable polymer is provided by polypentenamer, an elastomer similar to butadiene rubber. Monomer and polymer are in a metathesis equilibrium, see Eq. (1). Production of the polymer from the monomer (*r*ing *o*pening *m*etathesis *p*olymerization, abbreviated ROMP) and the degradation of the polymer to the monomer are possible under similar operating conditions.



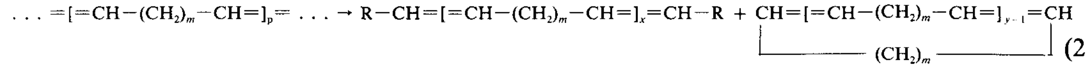
$$p \quad \rightleftarrows \ldots =[=CH-(CH_2)_3-CH=]_p= \ldots \tag{1}$$

This paper reconsiders another application of metathesis degradation, namely structure investigation of polymeric materials, with characteristic examples. It is concerned with the application to laboratory problems for the solution of analytical questions. What is meant here is degradation of unsaturated polymers by means of cross-metathesis with low-molecular-weight olefins. To facilitate discussion we employ MUP as an abbreviation for the *m*etathesis of *u*nsaturated *p*olymers. MUP degradation has been investigated for more than 20 years; the topic is dealt with in some review articles [4–6].

1.2. Analysis of Low-Molecular-Weight Degradation Products

1.2.1. Degradation to Low-Molecular-Weight Products

Where the low-molecular-weight products are to be analyzed, MUP degradation is carried out with symmetric olefins R—CH=CH—R (R = alkyl, preferably CH_3, C_2H_5, C_3H_7) to form linear products and cycles, see Eq. (2). In the linear products, the polymer units are inserted between the alkylidene groups R—CH= of the olefin; the units are considered from one double bond to the next. Classical metathesis catalysts such as tungsten hexachloride/tetramethyl tin are applied here even today. The low-molecular-weight products can be separated by gas chromatography (GC) and identified by mass spectrometry (MS).



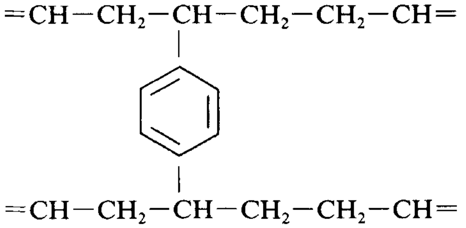
$$\ldots =[=CH-(CH_2)_m-CH=]_p= \ldots \rightarrow R-CH=[=CH-(CH_2)_m-CH=]_x=CH-R + \underbrace{CH=[=CH-(CH_2)_m-CH=]_{y-1}=CH}_{(CH_2)_m} \tag{2}$$

1.2.2. Investigation Methods in MUP Degradation Followed by GC/MS Analysis of the Degradation Products

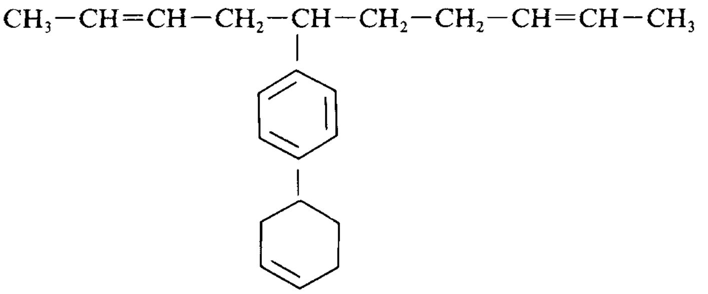
The usual evaluation methods of MS can be applied. Especially useful is ion search (recording of ion chromatograms) not only for the detection of the possible molecule ion but also for evidence of characteristic fragment ions. Chemical ionization may be helfpful in the case of products with larger molar masses where the molecule ion is not found in electron impact (EI) ionization. Interpretation of mass spectra is facilitated because the same unit occurs in different degradation products; if, for example, a cyclic degradation product exists, then it should be possible to find a corresponding linear product with the same unit. Many isomers cannot be distinguished by MS but by their different retention time in GC. For trace analysis, concentration of the substance in question is necessary. This is normally carried out by evaporation of the solvent in the reaction mixture.

A special method is evidence of the number of alkylidene groups in the degradation product. Degradation is carried out in separate experiments with different olefins, e.g., 2-butene and 3-hexene. As an example, crosslink **1** in poly(butadiene-

co-1,4-divinylbenzene) is considered [7]. Degradation with 2-butene (containing alkylidene groups $CH_3{-}CH{=}$) leads to product **2** with the molar mass 294 (besides other substances). Degradation with 3-hexene (containing alkylidene groups $C_2H_5{-}CH{=}$) gives the analogous product **3**, molar mass 322. The difference is $322 - 294 = 28$, corresponding to two methylene groups. This provides an unambiguous proof that products **2** and **3** contain two alkylidene groups of the low-molecular-weight olefin.



1



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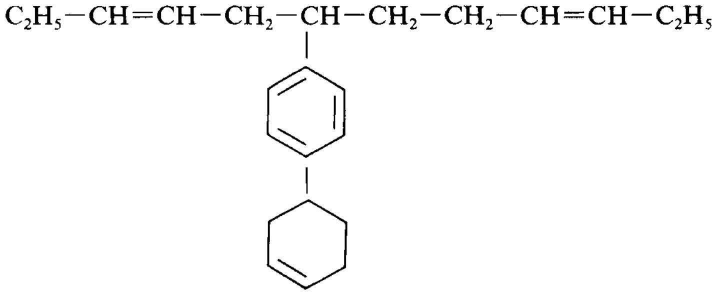

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1.2.3. Comparison of Investigation by Means of MUP Degradation to Low-Molecular-Weight Products with Spectroscopic Methods

Structure analysis via MUP degradation is not in competition with spectroscopic methods, it is a supplementary method. For NMR and IR spectroscopy, the polymers should contain more than 1 mol% of the units under consideration to give unambiguous results. Modern spectroscopy is also valuable in the range below 1 mol% in favorable cases. But its application fails if the polymer contains a large number of similar units in fractions below 0.5 mol% because of the superposition of the contributions of the different units.

There are many practical, interesting polymers that contain a number of different trace units; for example, copolymers where the formation is accompanied by minor side reactions, products of subsequent modification of polymers where various parallel reactions take place, or products with crosslinks in low concentration (e.g., rubber vulcanizates). The investigation of these products with spectroscopic methods has not been very successful as yet. Obviously, promising investigations can only be carried out where suitable investigation methods exist.

MUP degradation followed by identification of the degradation products by means of GC/MS is in principle suited for the investigation of these neglected structures, especially for multipolymers with a large number of different units in low concentrations, different crosslinks in lightly crosslinked polymers, or polymers with "defect" units (structural errors).

A limitation is that MUP degradation is only applicable to polymers with $-CH=CH-$ bonds in the backbone. Labile substituents (among others the hydrogen atoms in $-OH$, $-NH_2$, $-COOH$; $-Br$ in aliphatic structures) reacting with the catalyst or catalyst components are unfavorable. Investigation of (*Z*)/(*E*) isomerization is not possible. Spectroscopic methods are the methods of choice in these cases.

1.3. MUP Degradation to Soluble Polymers

Other applications of MUP, which can only be touched upon here, are based on the destruction of a cross-linked polymer matrix without determination of low-molecular-weight products. It is sufficient that the unsaturated polymer is rendered soluble. The cheap 1-olefins $CH_2=CH-R$ can be used for this purpose.

Some examples which can be useful for the solution of special problems have been described [6]: Surface etching by olefin metathesis is possible for subsequent investigation by means of electron microscopy; there should be two types of phase, one degradable by MUP and one not. Spectra are recorded with higher resolution from soluble polymers (obtained by MUP degradation) than from crosslinked polymers. The activity of metathesis catalysts has been measured by following the rate of the degradation of a crosslinked matrix; the activity measurement is reduced to a weight measurement for a gravimetric method.

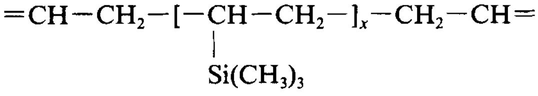
Some other applications have more general interest. Investigation of polymer blends is possible in suitable cases [8]; for example, if a phase without double bonds is dispersed in a phase with double bonds. The determination of fillers in the crosslinked matrix has also been described [9]. An advantage is that fillers can be determined which in other methods (for example, burning, ashing) are destroyed together with the polymer matrix.

2. RESULTS AND DISCUSSION

2.1. An Example of GC/MS Analysis: Investigation of Copolymers of Butadiene with Comonomers Containing Silicon

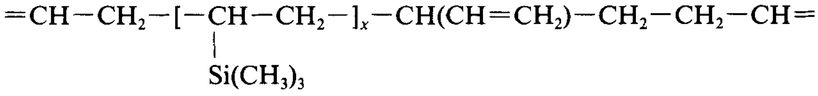
2.1.1. Units in Copolymers

A well-known application is the investigation of sequences in copolymers of butadiene. This can be present in 1,4-polybutadiene and 1,2-polybutadiene units. As an example, the degradation of poly(butadiene-*co*-trimethylvinylsilane) [10] is discussed here. The monomer trimethylvinylsilane is abbreviated TMS, 1,4-linked butadiene as 1,4B, and 1,2-linked butadiene as 1,2B. There are various types of units containing TMS. In **4**, TMS (*x* times) is located between two 1,4B. In **5**, the sequence is 1,4B, TMS (*x* times), 1,2B, 1,4B.



$$=CH-CH_2-[-\underset{\underset{\mathrm{Si(CH_3)_3}}{|}}{CH}-CH_2-]_x-CH_2-CH=$$

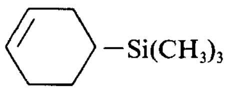
4



$$=CH-CH_2-[-\underset{\underset{\mathrm{Si(CH_3)_3}}{|}}{CH}-CH_2-]_x-CH(CH=CH_2)-CH_2-CH_2-CH=$$

5

Examples of MUP products are discussed here for degradation with 2-butene. From unit **4** ($x = 1$), the products 4-trimethylsilylcyclohexene (**6**) and 5-trimethylsilyl-2,8-decadiene (**7**) are obtained; in the metathesis equilibrium, only **6** occurs. A typical degradation product of unit **5** ($x = 1$) is 6-(2-cyclopentenyl)-5-trimethylsilyl-2-hexene (**8**). Interesting is the homologous series of products obtained from units **4** with $x = 1, 2, 3, 4$, etc. which have the structure **9** and occur in fractions decreasing with x. They were identified by GC/MS up to $x = 7$. This sequence corresponds to a chain of 22 C-atoms. Investigation should be possible for much longer chains by LC/MS coupling. In the investigation of low concentrations of such long sequences, MUP degradation is definitely superior to NMR spectroscopy.



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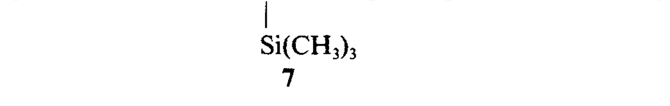
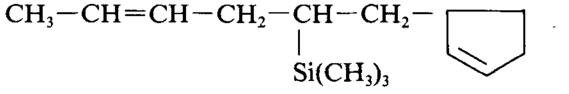


$$CH_3-CH=CH-CH_2-\underset{\underset{\mathrm{Si(CH_3)_3}}{|}}{CH}-CH_2-CH_2-CH=CH-CH_3$$

7



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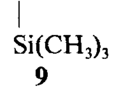
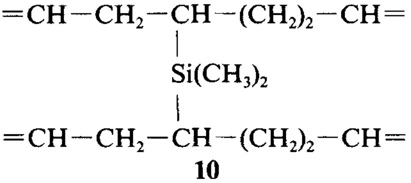


$$CH_3-CH=CH-CH_2-[-\underset{\underset{\mathrm{Si(CH_3)_3}}{|}}{CH}-CH_2-]_x-CH_2-CH=CH-CH_3$$

9

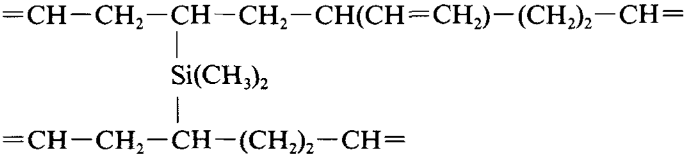
2.1.2. Crosslinks in Copolymers

An example is provided by copolymers from butadiene and dimethyldivinylsilane (MVS) [11]. In crosslink **10**, both chains have the sequence 1,4B, MVS, 1,4B. In crosslink **11**, the sequence in the upper chain is 1,4B, MVS, 1,2B, 1,4B. In crosslink **12**, this sequence is 1,4B, 1,2B, MVS, 1,2B, 1,4B. In the MS investigation of metathesis products of crosslink **12**, some evidence was also found for an isomeric unit with head-head addition, see unit **13**.



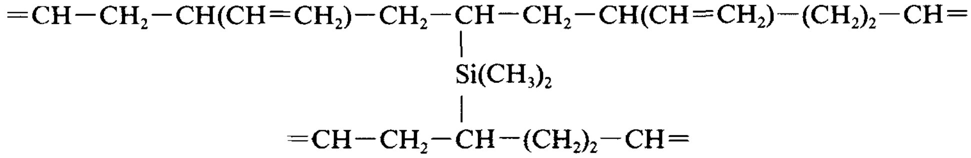
$$\begin{array}{l} =\mathrm{CH{-}CH_2{-}CH{-}(CH_2)_2{-}CH{=}} \\ \qquad\qquad\quad | \\ \qquad\qquad\;\; \mathrm{Si(CH_3)_2} \\ \qquad\qquad\quad | \\ =\mathrm{CH{-}CH_2{-}CH{-}(CH_2)_2{-}CH{=}} \end{array}$$

10



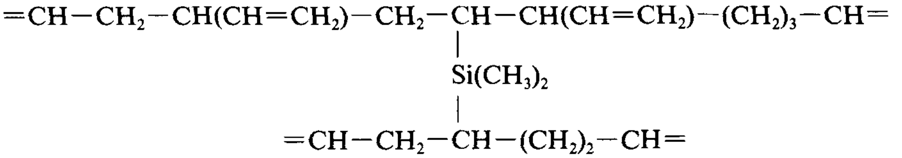
$$\begin{array}{l} =\mathrm{CH{-}CH_2{-}CH{-}CH_2{-}CH(CH{=}CH_2){-}(CH_2)_2{-}CH{=}} \\ \qquad\qquad\quad | \\ \qquad\qquad\;\; \mathrm{Si(CH_3)_2} \\ \qquad\qquad\quad | \\ =\mathrm{CH{-}CH_2{-}CH{-}(CH_2)_2{-}CH{=}} \end{array}$$

11



$$\begin{array}{l} =\mathrm{CH{-}CH_2{-}CH(CH{=}CH_2){-}CH_2{-}CH{-}CH_2{-}CH(CH{=}CH_2){-}(CH_2)_2{-}CH{=}} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\;\; \mathrm{Si(CH_3)_2} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad =\mathrm{CH{-}CH_2{-}CH{-}(CH_2)_2{-}CH{=}} \end{array}$$

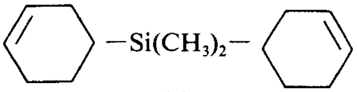
12



$$\begin{array}{l} =\mathrm{CH{-}CH_2{-}CH(CH{=}CH_2){-}CH_2{-}CH{-}CH(CH{=}CH_2){-}(CH_2)_3{-}CH{=}} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\;\; \mathrm{Si(CH_3)_2} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad =\mathrm{CH{-}CH_2{-}CH{-}(CH_2)_2{-}CH{=}} \end{array}$$

13

The degradation with 4-octene is described here. Typical degradation products of crosslink **10** were bis(3-cyclohexenyl)silane (**14**) and 7-(3-cyclohexenyl)dimethylsilyl-4,10-tetradecadiene (**15**). A degradation product of crosslink **11** is 1-(2-cyclopentenyl)-2-(3-cyclohexenyl)dimethylsilyl-4-octene (**16**). Product **17** is obtained from crosslink **12**. The decision between products from crosslink **12** or **13** is in principle possible by means of MS fragmentation. This is a problem of the reliability of MS methods.



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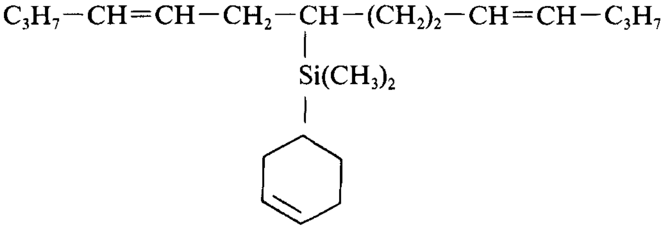

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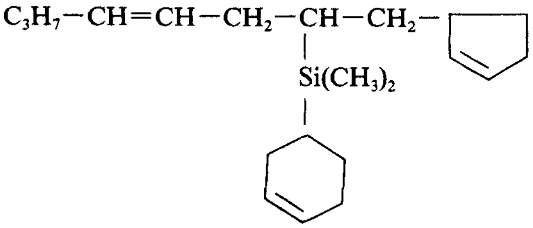

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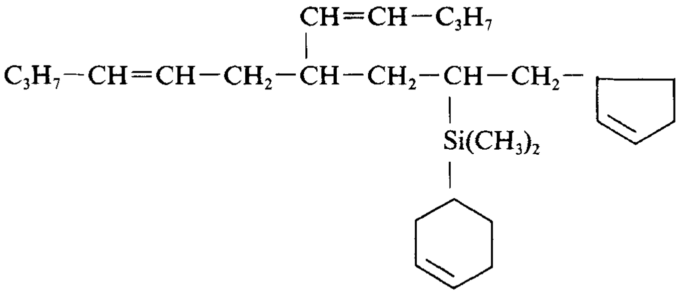


17

2.2. A Further Example of GC/MS Analysis: Investigation of Poly(Butadiene-*alt*-Propene) and Its Modification Products

2.2.1. Defects in Alternating Copolymers

MUP degradation is a powerful method to identify deviations (defects) in the ideal structure of alternating copolymers of butadiene and similar alternating copolymers. Our example, poly(butadiene-*alt*-propene), has the structure **18** and contains units **19**.

$$\ldots -CH_2-CH{=}CH-CH_2-CH(CH_3)-CH_2-CH_2-CH{=}CH-CH_2- \ldots$$

18

$$=CH-CH_2-CH(CH_3)-CH_2-CH_2-CH=$$

19

In addition to units **19**, ~1 mol% butanediylidene units **20** from 1,4-polybutadiene sequences were found in MUP degradation products. In the range of 0.5 mol% and below, units **21** and **22**, attributable to 1,2-addition of butadiene, were found. Units **23** with $x = 2$ or 3 showed propene sequences. Trace unit **24**, present with less than 0.1 mol%, gives evidence of the polymerization of the butadiene vinyl groups in two different chains. This leads to branching. With units **23** ($x = 2$) and **24**, cyclization to cyclooctene derivatives in the course of MUP degradation [12] was found. The other degradation products had structures analogous to those described in Section 2.1.1.

$$=CH-CH_2-CH_2-CH=$$

20

$$=CH-CH_2-CH_2-CH(CH=CH_2)-CH_2-CH=$$

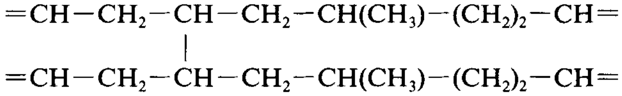
21

$$=CH-CH_2-CH(CH=CH_2)-CH_2-CH(CH_3)-(CH_2)_2-CH=$$

22

$$=CH-CH_2-(CH(CH_3)-CH_2)_x-CH_2-CH=$$

23



$$\begin{array}{l} =CH-CH_2-CH-CH_2-CH(CH_3)-(CH_2)_2-CH= \\ \qquad\qquad\qquad\;| \\ =CH-CH_2-CH-CH_2-CH(CH_3)-(CH_2)_2-CH= \end{array}$$

24

2.2.2. Subsequent Introduction of Substituents, Coupled with Partial Double Bond Shift

We discuss here the example of poly(butadiene-*alt*-propene) with units **19**, subsequently modified with an alkyl benzene [13]. The first step is hydrogen abstraction in the allyl position whereby a mesomeric allyl radical is formed. Abstraction is carried out with radicals formed in the thermal decomposition of dicumyl peroxide. The next step is addition of substituted benzyl radicals R′ to the allyl radicals. Now we have four different substituted units **25** to **28**.

$$=CH-CHR-CH(CH_3)-CH_2-CH_2-CH=$$

25

$$=CH-CH_2-CH(CH_3)-CH_2-CHR'-CH=$$

26

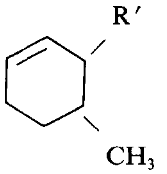
$$=CH-CH_2-CH(CH_3)-CH_2-CH_2-CHR'-CH=$$

27

$$=CH-CHR'-CH_2-CH(CH_3)-CH_2-CH_2-CH=$$

28

In MUP degradation, units **25** and **26** form substituted cyclohexene rings. Similarly, units **27** and **28** form substituted cycloheptene rings. Each of the four degradation products occurs in a *cis*- and a *trans*-isomer. The eight degradation products **29** to **36** result.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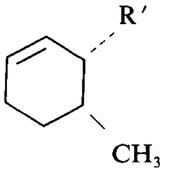
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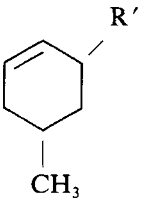
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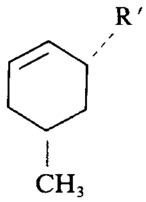
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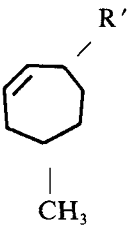
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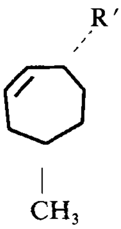
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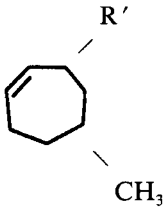
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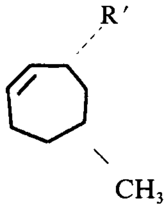
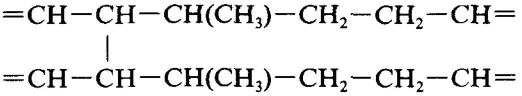

36

Substitution coupled with partial double bond shift has been investigated in detail in the case of 1,4-polybutadiene [4–6]. The abstraction of hydrogen from the primarily substituted units leads to further new units, hundreds of different units subsequently being formed. Until now, only units with one and two substitutents have been evidenced experimentally, but the fractions of all units occurring have been calculated by means of computer simulation (Monte Carlo calculation) [14]. In certain cases, the calculated results matched quite well with the results obtained via MUP degradation [6].

2.2.3. Subsequent Crosslinking, Coupled with Partial Double Bond Shift

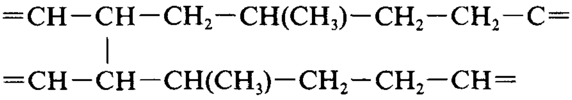
We investigated a two-step crosslinking reaction [15]. Poly(butadiene-*alt*-propene) was partially brominated in allyl positions with *N*-bromosuccinimide to give the units **25** to **28** with R = Br. The brominated polymer was treated in solution with zinc dust. Some gel resulted, corresponding to crosslinking.

The discussion is limited here to some characteristic structures. Crosslinks without double bond shift (example **37**, corresponding to two units **25**) and crosslinks with double bond shift in one chain (example **38**, corresponding to units **25** + **28**) were found.



$$\begin{array}{l}=\mathrm{CH{-}CH{-}CH(CH_3){-}CH_2{-}CH_2{-}CH{=}}\\ \qquad\quad |\\ =\mathrm{CH{-}CH{-}CH(CH_3){-}CH_2{-}CH_2{-}CH{=}}\end{array}$$

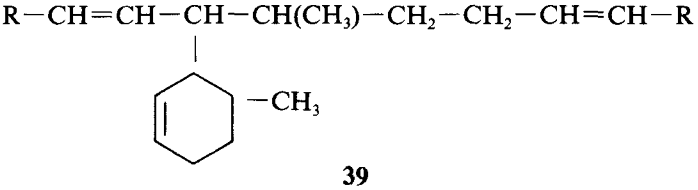
37



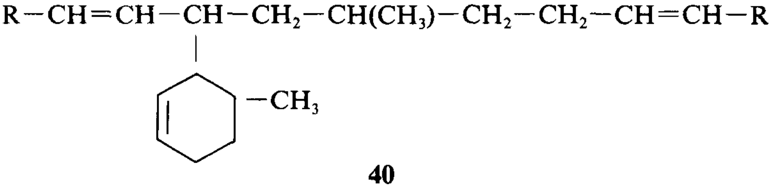
$$\begin{array}{l}=\mathrm{CH{-}CH{-}CH_2{-}CH(CH_3){-}CH_2{-}CH_2{-}C{=}}\\ \qquad\quad |\\ =\mathrm{CH{-}CH{-}CH(CH_3){-}CH_2{-}CH_2{-}CH{=}}\end{array}$$

38

Substance **39** is an example of a MUP degradation product of crosslink **37**. Substance **40** results from crosslink **38**.



39



40

Subsequent crosslinking by direct combination of the two polymer chains has also been observed in the reaction of brominated units of poly(butadiene-*alt*-propene) with Grignard compounds [16].

2.3. MUP Degradation of a Crosslinked Polymer Matrix: Determination of Carbon Black in Crosslinked *cis*-1,4-Polyisoprene (natural rubber)

The determination of carbon black fillers in vulcanizates of *cis*-1,4-polyisoprene (natural rubber, NR) is described here only as an example of this type of application. MUP degradation of NR to low-molecular-weight products is difficult because metathesis of substituted double bonds —CR=CH— is a very slow process [1].

The determination of carbon black in NR vulcanizates using MUP degradation has only recently been performed [15]. Attempts to degrade NR vulcanizates with the catalyst $WCl_6-(CH_3)_4Sn$ were not successful because the degradation rate was zero or insufficient. MUP degradation was possible with the catalyst $WCl_6-C_2H_5AlCl_2$. But this catalyst could not be used for carbon black determination because nonremovable layers of polymeric products without double bonds and decomposition products of catalyst components were formed on the filler particles.

TABLE 1. Determination of Carbon Black in a Polyisoprene Matrix Crosslinked with 0.5 g Dicumyl Peroxide/100 g Rubber (*s* = standard deviation)

	Carbon black, wt% ± *s*	
Carbon-black type	Calculated	Found
N 220	25.35	25.81 ± 0.35
N 330	25.53	25.45 ± 0.05
N 550	24.17	23.98 ± 0.12

A suitable catalyst is $WCl_6-(C_2H_5)_3Al_2Cl_3$. 1-Octene has been used as a low-molecular-weight olefin for degradation. The carbon black was separated by means of centrifuging. A series of washing processes with solvents such as chlorobenzene, methylene chloride, and ethanol and solvent mixtures were decisive for the accuracy of carbon black determination. Some characteristic results are shown in Table 1. In addition, the metathesis catalyst $WCl_6-(C_2H_5)_3Al_2Cl_3$ has a double bond shift activity. For this reason it is assumed that unsubstituted double bonds $-CH=CH-$, which can be cleaved in MUP reactions, are formed at least to a low percentage, see Eq. (3). The main final product of MUP degradation was a kind of cyclized rubber, well-known from the reaction of NR with strong acids.

$$\ldots -C(CH_3)=CH-CH_2- \ldots \rightarrow \ldots -CH(CH_3)-CH=CH- \ldots \quad (3)$$

3. CONCLUSIONS

When MUP degradation started, the GC/MS investigation of low-molecular-weight products was limited to those with molar masses below 500. But recent developments in MS and its coupling with liquid chromatography permit identification of products with far higher masses. For this reason it is thought that the real breakthrough of MUP degradation to low-molecular-weight products as an analytical investigation method is still to come. The development of sufficiently active new catalysts which are virtually free from side reactions will also be helpful.

For a broader application of methods using MUP degradation of a crosslinked polymer matrix to soluble polymers, the development of metathesis catalysts with special properties would be useful. For example, highly active catalysts which are indifferent to water, atmospheric oxygen, and impurities would open new fields of application.

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