POLYMER DEGRADATION BY CROSS METATHESIS

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<u>Abstract</u> - Olefin metathesis has been used since about 1969 for structural investigations in the field of polymers with C=C double bonds located in the backbone. In most cases polymers are degraded to low molecular substances which are separated by gas chromatography and identified by mass spectrometry. The method is especially useful in the investigation of modification and cross-linking reactions of polyalkerylenes which result in multipolymers with a large number of different structure units. Here it is in special cases superior to spectroscopic methods. Scope and limits of application, general principles and characteristic examples of the method are discussed.

INTRODUCTION

It is obvious that investigation of the structure of polymers is in many cases considerably more difficult than the investigation of the structure of low molecular substances. This is one of the reasons for the application of degradation methods in polymer analysis including a characterization of the low molecular degradation products. The main handicap of such degradation methods is that one can determine only the sequence of polymer units in the degradation products but not in the original polymer backbone. However one receives information relating to the structure of the polymer segment between the cleavage points.

The method which is summarized here is polymer degradation by olefin metathesis followed by a separation of the degradation products by gas chromatography and identification by mass spectrometry. Olefin metathesis is a redistribution reaction of alkylidene groups catalyzed by special transition metal compounds. As an example Eq. 1 shows the degradation of 1,4-polybutadiene by metathesis with a symmetrical olefin. The polymer is degraded to linear and cyclic products.

$$\begin{array}{c} \dots = CH - (CH_2)_2 - CH = CH - (CH_2)_2 - CH = CH - (CH_2)_2 - CH = \dots \\ & \downarrow + R - CH = CH - R \\ & \downarrow + catalyst \\ R - CH = CH - (CH_2)_2 - CH = CH - R \\ + CH = CH - (CH_2)_2 - CH = CH \\ & \downarrow \\ & - (CH_2)_2 - CH = CH \\ & \downarrow \\ & - (CH_2)_2 - CH = CH \\ & \downarrow \\ & - (CH_2)_2 - CH = CH \\ & \downarrow \\ & - (CH_2)_2 - CH = CH \\ & \downarrow \\ & - (CH_2)_2 - CH \\ & \downarrow \\ & - (CH_2)_2 - CH \\ & \downarrow \\ & - (CH_2)_2 - CH \\ & \downarrow \\ & p = 2, 3, 4 \\ & \dots \end{array}$$
(1)

Olefins R-CH=CH-R suitable for polymer degradation are especially 2-butene (Ref.1 & 2), 3-hexene (Ref.3 & 4) and 4-octene (Ref.5 & 6). In addition there were used ethylene (Ref.7), 5-decene, 6-dcdecene(Ref.8) and 7-tetradecene (Ref.9). Some catalysts are $WCl_6/C_2H_5AlCl_2$, $WCl_6/C_2H_5AlCl_2/C_2H_5OH$, $WCl_6/(iso-C_4H_9)_2AlCl$, $WCl_6/(CH_3)_4Sn$, $WCl_6/(C_2H_5)_4Sn/(C_2H_5)_2O$, $WCl_6/(CH_3)_2Si-CH_2-Si(CH_3)_2$ (Ref.10) and special tungsten complexes.

Oxygen atoms in the catalyst or the addition of small amounts of oxygen containing substances can increase the activity. But for practical polymer degradation they are not always necessary because the polymers and the other components of the reaction mixture contain enough unavoidable impurities which can accelerate the reaction.

Olefin metathesis has been applied to analytical purposes in the polymer field since about 1969 (Ref.11). In addition to our research group one should mention especially an early contribution by Michajlov and Harwood (Ref.1) in Akron and the work of Canji (Hamburg). Ast, who was a member of our group until 1973, continued work together with Kerber (Murich).

ADVANTAGES OF THE METHOD

At first we have to discuss the really practical advantages of polymer degradation by olefin metathesis followed by a characterization of the low molecular products.

Newadays it is well accepted that spectroscopic methods (IR, Raman, ¹H NMR, ¹C NMR etc.) are the most valuable tools for the investigation of the chemical structure of polymers. But each spectrum summarizes contributions of the participating structure sub-units. So it is quite clear that the interpretation of spectra will become difficult for copolymers with a large number of different structure units ("multipolymers") and especially if some structure units are very similar to each other (e.g. isomeric) and are present in a low quantity. Below there is a model of a cross-linked multipolymer (— = chain; \bullet = cross-link; A = substituent in a cross-link; B = substituent as a terminal group; C = substituent in a chain; D, E = pendant substituents) :



Such multipolymers with small amounts of special structure units result from many modification and cross-linking reactions used in technical processing of polymers, e.g. vulcanization of polymers. It is quite clear that the resulting structures are not fully understood from spectroscopic investigation. In these cases characterization of degradation products should be more significant.

Olefin metathesis can be applied only to polymers with incorporated C=C double bonds. Here for a long time ozonization was the investigation method of choice. However in ozonization the structure units are chemically changed as oxygen atoms are introduced into the degradation products; this degradation is irreversible. There was therefore the need for a degradation method in which the structure units of the polymer remain unchanged, at least in ideal cases, that is if side reactions are excluded. This requirement is met by olefin metathesis. In principle the polymers can be reconstructed from metathesis degradation products by a metathesis polycondensation (Ref.12 & 13) or a ring opening polymerization. This can also be interesting in regard to the recycling of polymer wastes.

DISTINCTION BETWEEN ISOMERIC ALKANEDIYLIDENE UNITS

In order to demonstrate the usefulness of metathesis degradation in structure investigations, some examples concerning structure isomerism ought to be discussed in a general way. At first one should consider isomeric polymer structures, for which it is easy to distinguish the metathesis degradation products by means of the varying molecule ions of the mass spectra. To this group belong :

a) differing copolymer sequences

$$= CH - CH_{2} + CH_{2} - CH_{2} + CH_{2} - CH = CH - CH_{2} + CH_{2} - CH_{3} + CH_{2} - CH = R_{1}$$

$$= CH - CH_{2} + CH_{2} - CH_{3} + CH_{2} - CH = CH_{2} + CH_{2} + CH_{3} + CH_{2} - CH_{3} + CH_{$$

b) ocurrence of structure units with one or with two substituents

and
$$=CH-CH-(CH_{2})_{m}-CH=CH-CH-(CH_{2})_{n}-CH=$$
$$=CH-CH-(CH_{2})_{m-1}CH-CH=CH-(CH_{2})_{n+1}CH=$$
$$=CH-CH-(CH_{2})_{m-1}CH=CH-(CH_{2})_{n+1}CH=$$

c) double bond shift

and

Secondly one must discuss isomeric polymer structures yielding metathesis degradation products which cannot be distinguished by their mass spectroidentification must take place by means of the varying mass spectrometric fragmentation and by means of the varying retention time in gas chromatography. In this group are to be found :

a) substituted polymer units with a different position of the substituent

$$= CH - (CH_2)_a - CH - (CH_2)_b - CH = and = CH - (CH_2)_{a-1} + CH - (CH_2)_{b+1} + CH = R_1$$

b) "backbone / side chain" isomerism

=CH-CH-(CH₂)_m-CH= (CH₂)_n CH₃ and

c) isomeric substituents

=CH-CH-(CH₂)_p-CH= and =CH-CH-(CH₂)_p-CH=
$$R_1$$
 iso- R_1

As an example for a different position of a substituent, degradation products of polymers with substituted octanediylidene units were examined by mass spectrometric fragmentation (Ref.14), e.g.

 $\begin{array}{l} {}^{H_{7}C_{3}-CH=CH-(CH_{2})_{2}-CH(C_{6}H_{5})-(CH_{2})_{3}-CH=CH-C_{3}H_{7}} \ [mass spectrum (EI) M^{+} (298), \\ {}^{M^{+}}-C_{3}H_{7} \ (255), M^{+}-C_{4}H_{9} \ (241), M^{+}-C_{7}H_{13} \ (201), M^{+}-C_{8}H_{15} \ (187)] \end{array}$ and

KINETICS OF THE DEGRADATION TO LINEAR PRODUCTS

For this investigation method it is necessary to degrade the polymer to low molecular products as completely as possible. Among other preconditions this is a kinetic problem.

$$CH-CH-(CH_2)_{m+1}$$
$$(CH_2)_{n-1}$$

The kinetics are simple only if in all stages of reaction the fraction of cycles can be neglected. This is the case in the degradation of 1,4-polybutadiene in solution in the presence of a large excess of low molecular olefin. Here only in the early stages of the reaction small quantities of cyclic oligomers (1,5,9,13-cyclohexadecatetraene, 1,5,9,13,17-cycloeicosapentaene etc.) and in the equilibrium traces of 1,5,9-cyclododecatriene can be found. Thus the polymer degradation can be described as a scission to linear products (Ref.15), Eq. 2.

(A) ...-CH=CH-...
+
$$\sim$$
 2 R-CH (C) (2)
(B) R-CH=CH-R

If all C=C double bonds in the chain react with equal probability the degradation is a statistical scission. The laws of such a statistical scission were first derived by Kuhn (Ref.16) for the hydrolysis of carbohydrates. They were adopted for metathesis degradation.

In the presence of a large excess of low molecular olefin the reaction proceeds to low molecular products

$$A + B \longrightarrow 2 C \tag{3}$$

and is a pseudomonomolecular reaction; k_1 = rate constant, t = reaction time, s = degree of degradation (number of the split double bonds/number of the original polymer double bonds).

$$-k_1 t = ln(1-s)$$
 (4)

In addition the total number n of polymer units in a degradation product at a given value of s can be calculated; w = weight fraction.

$$w_n = n s^2 (1 - s)^{n-1}$$
 (5)

An extended equation was derived for partially substituted polymers; in i units =CH-CHR-(CH₂)_m-CH= R' = substituent, in the other units R' = H, Ψ = degree of modification (Ref.17).

$$w_{n,i} = {n \choose i} n s^{2} (1-s)^{n-1} (1-\psi)^{n-i} \psi^{i}$$
(6)

Eq. 4 and 5 fitted the degradation of 1,4-polybutadiene with 4-octene quite well. Only in the initial period small deviations were found. In principle it is possible to detect a special degradation mechanism from non-fitting experimental data.

For modified 1,4-polybutadiene, Eq. 6, the probability of double bond scission in many cases was less in the neighbourhood of modified units. This was observed for polymers with partial addition of chlorine to the double bonds (Ref.6) and with partial substitution in \ll -position to the double bonds (Ref.18), where products with substituents were formed with a smaller rate than products with unmodified polymer units. A reason may be steric hindrance. The lower rate of degradation of polybutadiene with higher content of 1,2-addition compared with pure 1,4-polybutadiene can also be explained with a temporary blocking of the catalyst (Ref.4) by neighbouring vinyl groups in a "regenerative" transalkylidenation.

CHAIN LENGTH DISTRIBUTION OF LINEAR PRODUCTS

For the analytical application of polymer degradation by olefin metathesis it is desirable that only the smallest linear degradation product is formed, in the case of 1,4-polybutadiene R-CH=CH-CH₂-CH₂-CH=CH-R, but even with a large excess of R-CH=CH-R a series of products with different chain length is found, see Eq. 1. Preconditions for the derivation of the distribution functions are: formation of cycles may be neglected, all alkylidene groups and alkanediylidene groups combine with the same probability and the same equilibrium distribution is achieved in the formation of the polymer as in the degradation.

An example is given by the degradation of 1,4-polybutadiene with 6-dodecene

to products $CH_2-(CH_2)_4-CH \neq CH-(CH_2)_2-CH \neq CH-(CH_2)_4-CH_3$ (Ref.8). If one assumes a statistical combination of the fragments $CH_3-(CH_2)_4-CH=$ (abbreviated C6=) and $=CH-(CH_2)_2-CH=$ (abbreviated =C4=) the probability of the formation of a degradation product is proportional to the product of the mole fractions x of the combining alkylidene fragments and to the number of paths (n+1), on which the degradation product can be formed by combination of the alkylidene fragments (Ref.5 & 19).

$$x_{C6 \leftarrow C4} = x_{C6=}^{2} x_{C4=}^{n} (n+1)$$
 (7)

The generalized distribution function for a partially substituted polymer is Eq. 8 (Ref.17); A = alkylidene unit, B = unsubstituted polymer unit, C = substituted polymer unit.

$$\mathbf{x}_{n,i} = \begin{pmatrix} n \\ i \end{pmatrix} (n+1) \mathbf{x}_{C}^{i} \mathbf{x}_{B}^{n-i} \mathbf{x}_{A}^{2}$$
(8)

Eq. 8 is a variation of a Schulz-Flory distribution (Ref.20). It can only be valid if there is a statistical combination of the alkylidene units, that is to say an entropy determined reaction. The reaction enthalpy therefore should be zero, which cannot be exactly true in the degradation of polymers with different substituents.

It should be mentioned that according to Canji (Ref.3) the statistical chain length distribution is received only with low concentrations of the polymer. In metathesis reaction mixtures of polymer in higher concentration, special oligomerization equilibria may exist.

CYCLES AS INTERMEDIATES AND IN RING CHAIN EQUILIBRIA

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Till now we have discussed the particular case that the formation of cycles can be ignored. This is more or less an exceptional case. If the excess of low molecular olefin in 1,4-polybutadiene degradation is not very high, there are formed remarkable amounts of cyclic oligomers of the butanediylidene unit as mentioned before. Their concentration passes a maximum in the course of a reaction (Ref.9, 17 & 21). The question of the occurence of macro-cycles as intermediates of metathesis degradation needs further investigation. Cycles can be "cut out" of the polymer chains, Eq. 9. Especially in the case of a carbene mechanism of olefin metathesis a back-biting reaction can take place, Eq. 10 ((K) = catalyst). A larger cycle may react to two smaller cycles, Eq. 11.

$$\begin{array}{c} 1 & 2 & 3 & 4 \\ - \cdot - CH = CH - - - CH = CH - - - \end{array}$$

$$\begin{array}{c} 1 & 4 \\ - \cdot - CH = CH - - - \end{array}$$
 (9)

2 3/

$$(K) = CH \qquad (K) = CH \qquad (H = CH) \qquad (10)$$

$$(11)$$

$$(11)$$

$$(11)$$

$$(11)$$

$$(11)$$

$$(11)$$

$$(11)$$

In the metathesis equilibrium the cycles found are mainly small. For example in the case of the metathesis degradation of polypentenylene in the presence ${\tt PAAC54:2\ H}$

of a large excess of a low molecular olefin about 50% cyclopentene are found, the amount dependent on the experimental conditions (Ref.22).

The ring chain equilibria can be estimated by various methods. Empirical force field calculations were applied to the ring-chain equilibria including cyclopentenyl compounds, where enthalpy effects are important.



The value of the equilibrium constant K = $[a_F]/([a_D]\cdot[a_E])$ can be considerably reduced by the substituent R_1 : for $R_1 = H$, $K_{298} = 1,30$; for $R_1 = 9$ -phenanthryl, $K_{298} = 0,030$ (Ref.23)

Höcker (Ref.24) has calculated ring-chain equilibria for the range where the enthalpy effects may be ignored.

In any case it is useful to have at least a rough idea of the existing ringchain equilibria in the metathesis system investigated, because otherwise components are forgotten in the quantitative evaluation of the gas chromatograms for polymer analysis.

A special problem is the occurence of cyclic groups in the metathesis degradation of cross-linked polymers in the absence of low molecular olefins. Linear macromolecules with attached rings can be formed (Ref.25 & 26).

Or cycles can be cut off, resulting in a closer meshed network.

ADVANTAGES OF THE OCCURENCE OF CYCLES

In gas chromatographic polymer analysis after degradation by means of olefin metathesis it is often of advantage that in addition to linear degradation products cycles are formed as well. The cyclic degradation products have a lower mole mass than the corresponding linear degradation products with the same number of polymer units. Thus they can be separated by gas chromatography at lower temperatures and are easier to identify by mass spectrometry. Authentic substances for comparison with the degradation products (e.g. cyclopentenyl compounds) can be synthesized more easily than the corresponding linear products.

The degradation of polybutadiene which contains both 1,2 and 1,4 units results in the formation of cyclopentenyl and cyclohexenyl compounds (Ref.3 & 27)

 $= CH - CH_2 - CH_2 - CH = CH - CH_2 - CH_2$ (15)-CH=CH-R CH₂ CH₂-CH=CH-R linear degradation products

Cycles and bicyclic compounds should result from metathesis degradation of cross-linked products thus showing that there are cross-links (Ref.18 & 27).



It is easy to demonstrate double bond shift by means of cyclization of the newly-formed polymer units. For example the double bond shift in 1,4-polybutadiene results in the formation of cyclopentenyl compounds (Ref.28). Double bond shift in polypentenylene yields cyclohexenyl compounds.





LIMITATIONS OF POLYMER ANALYSIS

Side reactions of the catalyst

Side reactions result not only from the active catalyst species but also from components of the catalyst, from substances produced in the formation reaction of the active catalyst species and from decomposition products of the catalyst etc.

There are cationic reactions, which lead to a loss of double bonds of the higher molecular degradation products by cyclization (Ref.29 & 30).



Furthermore there are Friedel-Crafts reactions between aromatic solvents or substituents of the polymer and double bonds of the polymer, degradation products, low molecular olefin etc. Hydrochlorination products are formed with chlorine from the catalyst component WCl₆ (Ref.17). These hydrochlorination products can be produced before the metathesis step. One can see this from the product distribution. An example is the nearly complete degradation of 1,4-polybutadiene with 4-octene to 4,8-dodecadiene, but an unexpected large amount of degradation products with the unit =CH-(CH₂)_2-CHCl-(CH₂)_z-CH=. Another possibility is a hydrochlorination of a double bond which must have participated in a metathesis step, e.g. in the degradation of polyoctenylene with 4-octene the formation of the product 4-chloro-12-hexadecene. In mass spectrometrical identification these hydrochlorination products very often provide no molecule ion which corresponds to the products expected, but the molecule ion of an olefin which remains after splitting off the HCl. Products which have the mass spectrum of one and the same olefin then appear in different places of the gas chromatogram. In a quantitative evaluation of the gas chromatogram they must be calculated as hydrochlorination products.

Another reaction caused by the catalyst is cis/trans isomerization. This isomerization may be directly connected with metathesis.

Double bond shift caused by the metathesis catalyst is to be avoided by achieving the optimum of the reaction conditions. But this side reaction of the metathesis catalyst may be useful in the case of the degradation of polymers with substituted double bonds which do not take part in olefin metathesis without a shift, Eq. 19. This was investigated with the low molecular model compound 2-methyl-2-pentene (Ref.31).

^R 1 С=СН-СН ₂	$\stackrel{\text{R}}{\longrightarrow} \dots -\text{CH-CH=CH-}\dots$	
+ R-CH=CH-R	R1 CH-CH=CH-R + R-CH=CH	(19)

Difficult groups

The best results in polymer degradation by olefin metathesis are received with hydrocarbon polymer such as 1,4-polybutadiene, polypentenylene, polyoctenylene and with alkyl substituents as n-pentyl in the methylene groups of the polymers. In these cases the polymer can be nearly completely recovered in form of low molecular degradation products. It is only necessary to find the best reaction conditions in order to avoid side reactions and to reach the metathesis equilibrium. Polymer degradation can also be carried out in a satisfactory way in the presence of many substituents containing aromatic groups, halogen (Ref.29 & 32), oxygen and sulphur (Ref.33). Olefin metathesis with nitrogen containing substances is possible but less satisfactory (Ref.34 & 35).

A limitation in the general application of the method is that the metathesis degradation can be disturbed by groups which contain ionisable hydrogen such as -OH and -COOH. There are, however, possibilities to degrade polymers containing these "difficult" groups by olefin metathesis. One can apply the catalyst in a molar quantity comparable to the molar quantity of the functional groups considered (Ref.36). In this case at least the parts of the macromolecules can be determined in the form of low molecular degradation products which do not contain the difficult groups. But the use of a large quantity of the desired products are low.Another possibility is to make derivatives of the difficult groups. Thus a carboxylic group can be transformed to the ester group and a hydroxy group to an ether group; these disturb the olefin metathesis less. A problem is the complete conversion to the derivative.

Preparation of derivatives is also appropriate in the case of labile atoms such as bromine in allyl position, where an exchange with an alkyl or aryl group can be carried out before olefin metathesis (Ref.37).

$$\xrightarrow{\text{CH}-\text{CH}-\text{CH}_2-\text{CH}=} \xrightarrow{\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=} \xrightarrow{\text{CH}=\text{CH}_2-\text{CH}=} \xrightarrow{\text{CH}=} \xrightarrow$$

TRACE RANGE

The further one moves to the trace range of the gas chromatograms of metathesis mixtures, the more products are found. Each component alone is present in a quantity which could be ignored, but the total amount of all these products cannot be ignored in quantitative analysis. In addition minor by-products are especially interesting in the investigation of reaction mechanisms.

The great number of compounds results from chain length distribution, ring size distribution, structure isomers, stereo isomers, units of the polymer which are present in a low quantity, side reactions of the metathesis catalyst etc.

For a quantitative evaluation of the gas chromatograms as many of these trace compounds as possible must therefore be identified. One has to take into account which structure units of the original polymer occur and how many of them are present in one molecule of the trace compound. Good separation (capillary columns in gas chromatography) is necessary. Gas chromatographs and mass spectrometers with data processing facilities are of advantage. The whole equipment should be sophisticated.

APPLICATIONS

Sequences in copolymers

When structure units without double bonds exist, it is possible to determine sequences of these polymers. Blocks of a few units can be separated by gas chromatography. But it is obvious that products with larger blocks cannot be separated by gas chromatography. Then the method of choice is liquid chromatography (HPLC). In principle one can introduce units without double bonds in two ways :

a) Sequences caused by copolymerization

As examples one can quote copolymers of 1,3-butadiene and vinyl monomers. The investigation of the structure of butadiene-styrene copolymers was one of the first applications of the gas chromatographic polymer analysis after degradation by olefin metathesis (Ref.1)



A large number of linear and cyclic degradation products are to be expected in the metathesis degradation of butadiene-styrene copolymers with varying sequences of 1,4- and 1,2-polybutadiene units (Ref.38), e.g. (S = styrene):



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Copolymers of butanediylidene units and octanediylidene units substituted in 4- and 5-position were received by addition reactions of the C=C double bonds of 1,4-polybutadiene and investigated by metathesis degradation

$$1,4-\text{polybutadiene} \xrightarrow{H_2} \dots = CH-(CH_2)_6-CH=\dots (Ref.39 \& 40)$$

$$\xrightarrow{Cl_2} \dots = CH-(CH_2)_2-\overset{CH-CH-(CH_2)}{2}-CH=\dots (Ref.6 \& 29)$$

$$\xrightarrow{HCl} \dots = CH-(CH_2)_2-\overset{CH-CH-(CH_2)}{2}-CH=\dots (Ref.41)$$

$$\xrightarrow{Br_2} \dots = CH-(CH_2)_2-\overset{CH-CH-(CH_2)}{2}-CH=\dots (Ref.2 \& 29)$$

$$\xrightarrow{Br Br} Br$$

$$\xrightarrow{HBr} \dots = CH-(CH_2)_2-\overset{CH-CH-(CH_2)}{2}-CH=\dots (Ref.42)$$

$$\xrightarrow{(CH_2)} \dots = CH-(CH_2)_2-\overset{CH-CH-(CH_2)}{2}-CH=\dots (Ref.42)$$

$$\xrightarrow{(CCl_2)} \dots = CH-(CH_2)_2-\overset{CH-CH-(CH_2)}{2}-CH=\dots (Ref.43)$$

Reaction scheme of addition reactions $(+ X_2, e.g. + Cl_2)$:



The most important result of these investigations was that a partial addition to the double bonds in general does not lead to large blocks of saturated modified units. It rather yields statistical distribution along the polymer chain for which, under special preconditions, the distribution function is (j = size of the blocks, Ψ = degree of modification) (Ref.29 & 40) :

$$Z_{j} = (1 - \gamma)^{2} \gamma^{j} (j + 1)$$
⁽²³⁾

However investigations indicate that in some cases double bonds react with reduced probability in the immediate neighbourhood of double bonds which have already reacted. If less than 50% of the double bonds have reacted there is then a distribution of the structure units which is between the distribution of a statistical copolymer and a double alternating copolymer.

$$= \frac{X X}{I} = \frac{$$

double alternating copolymer

Modification by Grignard-Wurtz reactions

A modification reaction which could be investigated satisfactorily by metathesis degradation was Grignard-Wurtz reaction of partially brominated polyalkenylenes (1,4-polybutadiene, polypentenylene, polyoctenylene). The bromine was introduced with N-bromosuccinimide (NBS) in α -position and by addition of HBr to the double bonds. A reaction with magnesiumorganic compounds was carried out subsequently (Ref.44 & 45). It was possible to investigate the dependence of the Grignard-Wurtz reaction and the metathesis reaction on the structure of the substituent.



In the case of α -bromination of 1,4-polybutadiene followed by a reaction with phenylmagnesium bromide there was observed a double bond shift in association with double substitution, yielding =CH-CH(C₆H₂)-CH₂-CH(C₆H₅)-CH= (Ref.46). Double bond shift was a side reaction in all Grignard-Wurtz reactions of α -brominated polyalkenylenes (Ref.28).

Simultaneous Grignard-Wurtz reactions were investigated by metathesis degradation. In the simultaneous reaction of phenylmagnesium bromide and benzylmagnesium bromide with &-brominated 1,4-polybutadiene there was found a preferential reaction of benzylmagnesium bromide (Ref.44).

Another aspect was the occurence of transfer reactions. If toluene was used as a solvent for Grignard-Wurtz reactions then benzyl groups were found in the polymer (Ref.14 & 44), Eq. 26. Similar transfer reactions were observed in the reaction of partially brominated 1,4-polybutadiene with lithiumorganic compounds (Ref.47).

 $\cdots = CH - (CH_2)_2 - CH = CH - CH_2 - CH = CH - (CH_2)_2 - CH = \cdots$ Br (26) $+ R_1 - MgBr$ toluene $\cdots = CH - CH_2 \cdots + \cdots = CH - CH_2 \cdots$ $R_1 \qquad CH_2 \\ C_6H_5$

Furthermore metathesis degradation was suitable for the detection of substituents introduced by Grignard-Wurtz reaction, which could be estimated only with difficulty by spectroscopic methods alone, e.g. small quantities of cyclohexyl groups (Ref.44 & 45).

Modification by free radical aralkylation

In this reaction 1,4-polybutadiene is dissolved in toluene or a substituted toluene and heated with dicumyl peroxide (or di-tert-butyl peroxide) as a radical source (Ref.48). According to metathesis degradation, aralkylation is the main reaction, Eq. 27 ($R_2^{\bullet} = C_6 H_5 - C(CH_3)_2 - 0^{\bullet}$ and CH_3^{\bullet} from the decomposition of dicumyl peroxide).



A partial double bond shift is involved in this modification reaction (Ref.28).

In the aralkylation with cumene a homolytic aromatic substitution was found as a minor side reaction by investigation of the metathesis degradation products ($P^* = polymer radical$) (Ref.27 & 49).

(28) (28) (28) (28)

Another side reaction was methylation by CH_3^{\bullet} radicals of the peroxide decomposition (Ref.32 & 50).



The aralkylation with 2-chloro-p-xylene resulted in the formation of two structure isomers. The corresponding metathesis degradation products with 4-octene were found in almost equal amounts (Ref.32).



Further investigation is needed to determine the extent to which addition reactions to the double bond of the polymer and hydrogen transfer reactions which include the double bonds are side reactions of free radical aralkylation. Metathesis reaction products were found in small amounts which indicate a hydrogenation, e.g.

$$\begin{array}{c} \dots = CH - CH_2 - CH_2 - CH = CH - CH_2 - CH_2 - CH = \dots \\ & \downarrow + R_1 \cdot \\ \dots = CH - CH_2 - CH_2 - CH - CH - CH_2 - CH_2 - CH_2 - CH = \dots \\ & R_1 \\ & \downarrow + H \\ \dots = CH - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH = \dots \\ & R_1 \end{array}$$
(30)

and a dehydrogenation, e.g.

$$\cdots = CH - CH_2 - CH_2 - CH = CH - CH_2 - C$$

CONCLUDING REMARKS

Till now we have only discussed applications of the analysis of low molecular products received after degradation by olefin metathesis.

One should mention other analytical applications : investigation of the structure of cross-linked polymers by metathesis degradation to soluble polymers which can be characterized (Ref.35 & 5%), determination of the insoluble residue of the degradation of highly cross-linked polymers which seems to be connected with the cross-link density (Ref.52), etching of the surface of cross-linked polymers for morphological investigations by electron microscopy (Ref.27 & 53), determination of fillers non-reactive in olefin metathesis by degradation of the surrounding cross-linked polymer (Ref.54) and measurement of the activity of metathesis catalysts by degradation of a cross-linked polymer in a surface reaction (Ref.55).

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