ANALOGOUS POLYMER REACTIONS, THEIR KINETICS AND ORGANIC CHEMISTRY

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INTRODUCTION

Organic reactions of high polymers have often been reported; in the recent reviews the various types of chemical reactions were examined both from the point of view of the reaction and the polymers. The present discussion is restricted to the more recently reported aspects of high polymer organic reactions covering successively organic reactions from the viewpoint of the influence of stereochemical structure of polymer, selectivity of the reactions and their analogy with reactions on homologous low molecular weight model compounds.

INFLUENCE OF STEREOCHEMICAL STRUCTURE OF POLYMER

Acrylic and methacrylic polymers

Reactions of high polymeric functions can be strongly influenced by neighbouring group effects. As soon as a polymeric reaction proceeds, a copolymer is formed of which the composition changes continuously, and in which the unreacted groups become progressively surrounded by new groups. If functional interactions occur between neighbouring groups, the reaction mechanism will be changed and the overall rate of reaction will be also progressively affected. A very simple example of this effect is found in the hydrolysis of polyacrylamide in buffered acid solution; as soon as the degree of conversion becomes three to five per cent, the reaction accelerates strongly. It is only in copolymers containing few units of isolated groups, that the environment remains constant and interpretation is more simple.

This was the case in the experiments described by Morawetz and co-workers on the hydrolysis of copolymers of acrylic or methacrylic acid with small proportions of p-nitrophenyl methacrylate; the rate of reaction is many orders of magnitude higher than that of the corresponding trimethyl acetic ester. It is admitted that the reaction proceeds intramolecularly through an acid anhydride intermediate formed by the attack of a neighbouring carboxylate on the carbonyl of the ester group. In the case of methacrylic acid copolymers, either with p-nitrophenyl methacrylate or p-nitrophenyl acrylate, two kinds of ester groups must, however, be admitted of which 18 to 28 per cent are about ten times as reactive as the remainder; the nature of the methacrylic chain, therefore exercises a strong influence on the course of the hydrolysis. From these data it becomes evident that immediate neighbourhood of reactive groups was not sufficient to explain the experimental
G. SMETS

facts, but that some other supplementary conditions are required, which are directly related to the structure of the polymeric chain.

Studies carried out on the hydrolysis of copolymers with relatively high content of both monomers, although more complicated, have all led to the same conclusion.

Copolymers of acrylamide and acrylic acid (acid content varying from 70 to 88 moles per cent) hydrolyse in buffered acid solutions in two steps, of which the first is about 50 to 100 times faster than the second. The rapid step results from the interaction of an amide group with an undissociated neighbour carboxyl group, while the slow step corresponds to the reaction of a polycrylamide unit with external acid. However, only about 40 per cent of the amide groups directly adjacent to an undissociated acid group hydrolyse rapidly; the other 60 per cent behave similarly to the slow amide groups with external acid.

In the case of the hydrolysis of partially neutralized methacrylic acid–methyl methacrylate copolymers the intramolecular reaction mechanism consists also in the interaction of an ester function of one side, and a carboxyl and/or a carboxylate neighbouring group of the other side. For copolymers with high acid content (72 per cent and more) at a degree of neutralization of 0·25, i.e. one carboxylate against three carboxyl groups, the rate of hydrolysis is maximum and about three times that at other degrees of neutralization. This maximum rate is characterized by a much lower activation energy, namely 16 kcal instead of 23 kcal and was interpreted in terms of a concerted reaction mechanism. The limited degree of conversion of the reaction is always appreciably lower than the calculated one, and corresponds to about 45 per cent of the ester group.

Similar results were also obtained with acrylic acid–ethyl ethacrylate copolymers; it was shown that only a part of the ester groups can be hydrolysed. The rate was directly proportional to the content of acid-ester-acid triads, and highest when the degree of neutralization was equal to 0·5, at which the activation energy is minimum (17 kcal/mole). The final degree of conversion corresponds to about 58 per cent of the acid-ester-acid triads.

All these data on the hydrolysis of acrylic and methacrylic polymers confirm the requirement that some stereospecific conditions should be fulfilled, besides the direct vicinality of the functions. In fact the formation of a 1,3-distributed six-membered cyclic intermediate in the course of reaction evidently depends on the relative position of the groups and, consequently, on the microtacticity of the polymeric chain. Because of the similarity in bond length of carbon–carbon and carbon–oxygen bonds as well as in the C–C–C and C–O–C angles, the stereochemistry of six-membered rings containing oxygen is similar to that of cyclohexane; consequently, the conclusions concerning 1,3-dialkyl cyclohexane derivatives will remain valid in the present discussion, although the participation of carbonyl–carbon atoms with $sp^2$ configuration slightly affects the structure of the hexatomic ring.

In 1,3-dimethyl substituted cyclohexanes, the cis-isomer (meso variety) corresponding to an isotactic structure, will be diequatorial because the interaction energy is negligible. A diaxial cis-conformation is particularly unfavourable because the substituents crowd each other strongly, and the
resulting steric interaction gives rise to an unfavourable energy term of 5.5 kcal/mole\textsuperscript{10}. The trans-isomer (\textit{dl}-racemic) corresponding to a syndiotactic structure, has always one substituent in equatorial, the other in axial positions, and presents two gauche CH$_3$/H interactions. It follows from these considerations that the \textit{cis}-diequatorial-isomer (isotactic) should be more stable by 1.8 kcal/mole than the axial-equatorial trans-isomer. In the case of a cyclized polycrylic anhydride intermediate, only one CH$_3$/H interaction exists on account of the ring oxygen and therefore the difference of stability can be evaluated to about 1 kcal; indeed, the conformational free energy differences for monosubstituted cyclohexanes (in kcal/mole) increase in the following order; methyl: 1.7, ethyl: 1.8; isopropyl: 2.1; and are about equal for n-propyl, n-butyl and neo-pentyl and estimated to be 2.0–2.1. As a consequence, in so far as intermediate cyclization is involved in the reaction mechanism, an isotactic polycrylic chain will be always more reactive than a syndiotactic one, because a diequatorially substituted ring is more easily formed. It can be represented as follows:

\begin{center}
\textbf{Reaction intermediate}
\end{center}

This interpretation has been verified by comparison of conventional and isotactic acrylic acid–methyl acrylate copolymers of about the same molar composition. The rates of hydrolysis, measured at 103°C in buffered solutions, show that the isotactic polymers hydrolyse 3 to 5 times more rapidly than the conventional polymers; moreover, the final degree of conversion is much higher\textsuperscript{8}. These data are summarized in Table 1.

In the methacrylic series, the intermediate six-membered ring is tetra-substituted in 1,1’ and 3,3’ due to the presence of the two chain segments and two methyl groups in \textit{z}-position with respect to the carbonyl group instead of two hydrogen atoms. With models it can be seen that there is always a considerable steric hindrance for each configuration; nevertheless, the isotactic polymer is the least hindered.

To our knowledge similar model homologous substances have not yet been studied quantitatively. However, it can be predicted that, on account of the steric interaction between the two axial substituents, formation of a cyclic
Table 1. Rate constants of hydrolysis of acid-ester copolymers of different tacticities

<table>
<thead>
<tr>
<th>Acid content (mole %)</th>
<th>$r = \frac{\text{acid carboxylate}}{\text{ester}}$</th>
<th>Apparent first order rate constants $\times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Conventional</td>
</tr>
<tr>
<td>A. Acrylic acid-methyl acrylate copolymers ($T^\circ$: 103°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>64.5 conven.</td>
<td>0</td>
<td>5.1</td>
</tr>
<tr>
<td>67</td>
<td>1</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.7</td>
</tr>
<tr>
<td>80.5 conven.</td>
<td>0</td>
<td>3.1</td>
</tr>
<tr>
<td>80</td>
<td>1</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.9</td>
</tr>
<tr>
<td>B. Methacrylic acid-methyl methacrylate ($T^\circ$: 110°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>50</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>60</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>72</td>
<td>0.9</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>78.3</td>
<td>1</td>
<td>5.3</td>
</tr>
<tr>
<td>83</td>
<td>1.1</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.0</td>
</tr>
</tbody>
</table>
| intermediate will be much more difficult than in the acrylic series. Indeed, as can be seen from Table 1, at the same degree of neutralization, the methacrylic copolymers always hydrolyse about 10–12 times slower than the acrylic copolymers of the same molar composition, if one takes into account the difference of reaction temperature for the two series of experiments (110°C instead of 103°C).

The isotactic methacrylic acid-ester copolymers obtained by partial acid hydrolysis of isotactic polymethyl methacrylate (prepared in toluene with Grignard reagent) hydrolyse four to five times more rapidly than the conventional copolymer; again a much higher degree of conversion can be obtained. Contrarily, low temperature radical polymerized methacrylate mainly of syndiotactic structure (prepared in the presence of UV light and benzoin as sensitizer) hydrolyses very slowly and, at high acid content, undergoes no detectable hydrolysis. For both isotactic and conventional copolymers, the hydrolytic rate is maximum at a degree of neutralization of 0.25; this fact confirms the intramolecular nature of a concerted reaction mechanism.

These data on acrylic and methacrylic copolymers demonstrate conclusively the importance of stereoisomerism in the intramolecular reaction of polymeric chains. When this intramolecular mechanism disappears in favour of a bimolecular mechanism with an external reagent, the reaction rate becomes determined mostly by the accessibility of the functions, and the order of reactivity may be reversed. In this sense the higher initial rate (about 20 times) of saponification of syndiotactic polymethyl acrylate with sodium
ANALOGOUS POLYMERS

hydroxide compound to that of several radical polymerized samples can be readily understood.

It is evident that the higher stability of the cis-1,3-diequatorial rings compared to the trans-axial equatorial is also responsible for the isomerization of syndiotactic polyacrylic anhydride by heating at 97°C for several hours in cyclohexanone or by polymerization in dimethylformamide; this equilibrium isomerization is related to the presence of the α-hydrogen atoms and involves enolization. Similarly, a definite increase in the percentage of isotactic character with an increase of polymerization temperature was found in the case of polymethacrylic anhydride.

The polymers obtained at relatively low temperatures show, after esteriﬁcation with diazomethane, a similar nuclear magnetic resonance spectrum to conventional polymethyl methacrylate; prepared at higher temperatures and low monomer concentration the spectra are similar to those of the isotactic polymer. Although it is admitted that cyclohexyl type radicals would be non-stereospeciﬁc, the syndiotactic structure is kinetically more readily formed, while the isotactic one is the thermodynamically more stable conﬁguration.

Evidently the validity of these stability considerations vanishes if a cyclic structure of the polymer is not involved; for an open chain an equilibrium conﬁgurational arrangement will correspond to a minimum of polarity and steric effects resulting from adjacent units. In this sense it can be expected that vinyl polymers carrying electron withdrawing substituents and containing α-hydrogen atoms will undergo epimerization and be transformed into their equilibrium arrangements. Such experiments have been carried out very recently on polyacrylic model substances, namely heptane 2,4,6-tricarboxylic acid, its salts and its methyl ester which were separated into

| Table 2. Stereoisomeric equilibrium for H—(CH₂—CH—)₃—CH₃ derivatives

<table>
<thead>
<tr>
<th>Ester epimerization (t°: 25°C) Alkoxide catalyst</th>
<th>Acid and salt epimerization (t°: 180°C) Aqueous solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>K</td>
</tr>
<tr>
<td>Me</td>
<td>1:47</td>
</tr>
<tr>
<td>Et</td>
<td>1:84</td>
</tr>
<tr>
<td>i.Pr.</td>
<td>3:40</td>
</tr>
</tbody>
</table>

K⁻ = (syndio) / (isot.)

their isotactic, heterotactic and syndiotactic isomers. The diastereomers were brought to a common equilibrium concentration either by heating their aqueous solutions at 180°C, or by treatment with alkoxide (for the esters). Similar experiments were carried out on isotactic rich synthetic mixtures (28: 57 : 15 iso, hetero, syndio) of ethyl and isopropyl heptane tricarboxylate. In all cases the syndiotactic form is favoured over the isotactic, and steric factors are more important than polarity effects. It is admitted that these equilibria determined on the models are a good first approximation of the corresponding equilibria for the acrylic polymers.
These data show also that care should be taken during the isolation and treatment of polyacrylic polymers, if one desires to correlate physical and chemical properties with the stereochimical structure.

In connection with these kinetic and thermodynamic data it is worthwhile to mention that the same stereoisomer concepts can be used for interpreting the ionization equilibria of polymeric acids, as a consequence of neighbouring group interaction.

For example, a strong potentiometric difference has been found between hydrolysed maleic anhydride–styrene and diethyl fumarate–styrene copolymers, the second being much weaker polycyads than the first. In the polycyad derived from maleic anhydride both carboxyl groups are in the cis-position, and due to the repulsion between the methylene and —CH—Ph—groups both carboxyls are near each other. Contrarily in the fumamic system, the carboxyls are in the trans position, and more distant and, consequently, are less acidic. The electrolyte behaviour of other maleic anhydride copolymers with several vinyl monomers has been also examined at different degrees of neutralization and interpreted in terms of coiling up of the chain and neighbourhood of carboxyl groups. With some comonomers, e.g. vinyl esters, the formations of a hydrogen bond between the ester and neighbour carboxyl groups could also modify the ionization constant and should therefore be taken into account.

The apparent acid dissociation constants of polymethacrylic acids depends also on the tacticity of the system; at a same degree of neutralization the isotactic polycyad solution has a higher pH-value than the syndio- and atactic acids; it is thus a weaker acid than the two others, which are equivalent.

**Polyvinyl acetals**

It was already observed previously that the kinetics of the hydrolysis of polyvinyl acetals differ considerably depending on the acidity of the reaction medium. While in N/3 sulphuric acid the rate of hydrolysis is proportional to the acetal concentration and independent of the concentration of alcohol, in more dilute solution it is strongly influenced by the neighbour hydroxyl groups, in such a manner that the rate is highest for polyvinyl acetals with highest alcohol content. This effect suggested an influence of chain microtacticity on the reaction rate, and on the equilibrium degree of hydrolysis. Indeed, recently, the rates of hydrolysis of several polyvinyl acetal samples of different tacticity have been reported; as the syndiotactic content of the original polyvinyl alcohol increases (as evaluated from the infrared absorbance ratio $D_{910}/D_{850}$) the acetal becomes more easily hydrolysable. Similarly the acetal derived from model compound $dl$-pentane-2,4-diol(syndiotactic), hydrolyses more easily than the acetal of the corresponding meso-diol (isotactic).

On the basis of the reversibility of the reaction the equilibrium degrees of acetalization have been examined as a function of the tacticity of the chain by heating at 60°C with 0.02N HCl; the results are reported in Table 3.

Dependence on tacticity shows that the syndiotactic varieties are the least stable, for the model compounds as well as for the polymers. Although
different factors may be taken as responsible for the different rates, e.g. influence of neighbour-hydroxyl groups, hydroxyl group association it seems, nevertheless, that the reactivity of the acetal ring itself is most important, at least for the first steps with highly acetalized samples. It is also noteworthy that isotactic polyvinylalcohol is more reactive in its acetalization with acetaldehyde and reaction with boric acid than the syndiotactic and conventional polyvinylalcohols, these two reacting at about the same rate.

Table 3. Equilibrium hydrolysis of various acetals\textsuperscript{27, 28}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Stereostructure</th>
<th>Degree of acetalization</th>
<th>$K$ equilibrium constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>Pentane-2,4-diol</td>
<td>Meso(isotactic)</td>
<td>100</td>
<td>86:33</td>
</tr>
<tr>
<td>Heptane-2,4,6-triol</td>
<td>Isotactic</td>
<td>85:4</td>
<td>66</td>
</tr>
<tr>
<td>Polyvinylalcohol</td>
<td>Isotactic</td>
<td>82:7</td>
<td>55:8</td>
</tr>
<tr>
<td>Polyvinylalcohol</td>
<td>Conventional</td>
<td>77:5</td>
<td>50:6</td>
</tr>
<tr>
<td>Pentane-2,4,6-triol</td>
<td>$dl$ (syndio)</td>
<td>100</td>
<td>49:8</td>
</tr>
<tr>
<td>Polyvinylalcohol</td>
<td>Syndiotactic</td>
<td>53:4</td>
<td></td>
</tr>
</tbody>
</table>

As in the previous case of the polyacrylic derivatives, this lower stability of the syndiotactic acetal results from the axial-equatorial-1,3 orientation of the chain segments in the six-membered ring; there are however in this case two chain hydrogen interactions (1:3 and 1:5) and two oxygen heteroatoms.

Polyvinyl acetate
The hydrolysis of polyvinyl acetate has been examined very carefully during the last years. Sakurada, Sakagushi and co-workers\textsuperscript{29, 30} noticed previously that the rate of this reaction increases autocatalytically with the degree of conversion, while the rate of acetylation decreases with an increasing degree of acetylation. In order to correlate such effects with the stereochemical configuration of the polymers, polyvinyl acetate samples of various tacticities have been hydrolysed in alkaline medium; they give almost the same S-shaped time-conversion curves. Hydrolysis of the esters is thus relatively insensitive to the tacticity of the polymers\textsuperscript{31}; the effect becomes only noticeable when isotactic sequence above some critical length are present. A smaller initial rate, but a stronger autocatalytic effect, was found by Sakurada, Sakaguchi and co-workers\textsuperscript{92} for isotactic polyvinyl acetate compared to the syndio-variety. Polyvinyl acetates prepared by radical polymerization in many different conditions are all equal and behave similarly to syndiotactic polyvinyl acetate, obtained from polyvinyl trifluoroacetate.
In any case, the differences between the isotactic and syndiotactic polyvinyl acetals are much less pronounced than in the hydrolysis of polyvinylacetals; this greater influence of chain tacticity on the hydrolysis of polyvinyl-acetals is essentially due to the presence of the six-membered rings which differ appreciably in stability depending on their tacticity. It could also be argued that likely intramolecular hydrogen-bonding occurs more easily for the acetal than for the ester, on account of the higher electron availability at the acetal oxygen, compared to that of the ester alkyl oxygen with its electron withdrawing carbonyl group. It is however admitted that this effect would be of minor importance compared to the ring stability effect. It is evident that these conclusions and the interpretation of results suppose a high chain regularity and a correct evaluation of the tacticity of the starting polymers. In the case of polyvinyl alcohol, the presence of small amounts of glycol units seems to be of minor importance \(^{33, 34}\); on the other hand, the high syndiotacticity of free-radical polyvinyl trifluoroacetate has been recently contested\(^{35}\), consequently, some of these previous conclusions should be accepted only with caution.

**Polyvinyl chloride**

The stability of polyvinyl chloride towards zinc metal as a function of the method of synthesis and, consequently, of the internal structure of the polymers was recently studied by Millan and Smets\(^{36}\). Emulsion and mass polymerized vinylchloride undergo rapid dechlorination and cyclopropane ring formation simultaneously; on the other hand, polyvinyl chloride, prepared in butyraldehyde solutions and characterized by a much higher percentage of syndiotactic arrangement, behaves differently. From a given reaction time the formation of double bonds becomes most important, and cyclopropane ring formation and dechlorination reaction disagree more and more; simultaneously the infrared absorption corresponding to the syndiotactic arrangement (604 cm\(^{-1}\)) disappears completely.

**SELECTIVITY OF ORGANIC REACTIONS**

From the preceding section, it becomes evident that determination of the stereochemical structure of polymers by means of only chemical methods even if it is possible must be very difficult. Most polymers contain different stereochemical arrangements in the same molecule, and the differences of reaction rates between these are insufficiently pronounced for making possible a quantitative determination of one structure besides the other ones. Furthermore, it is well known that high polymer chemical transformations very seldom proceed with a quantitative yield, not only because side reactions
occur or the solubility properties change, but very often because the electrical potential of the polymer molecule increases with increasing degree of conversion, with the result that the shape of the macromolecule and its reactivity are profoundly modified.

One should therefore, be extremely careful before coming to conclusions about attributing kinetic and organic effects to the internal structure of the polymer, and should realize that only very simple problems can be solved chemically.

The first problem related to chain structure in both vinyl polymers and copolymers, is the question of whether monomer units are arranged in a head-to-tail fashion, or head-to-head, tail-to-tail.

Although the main structure is predominantly of the alternate type, some vicinal addition occur with monomers of low reactivity as, e.g. vinyl acetate and vinyl chloride. Assuming that the accessibility of all the functions is equivalent and remains unchanged in the course of the reaction, Flory has theoretically predicted that the random removal of pairs of substituents of a polymeric chain results in the isolation of 13:5 and 18:4 per cent of the substituents for an alternate and statistical structures respectively, even if the reaction proceeds quantitatively for low molecular weight derivatives. Only a regular vicinal structure permits a theoretical 100 per cent removal, but this type of 1,2 polyvinyl polymer is unknown. On the basis of these predictions, it should theoretically be possible to evaluate the degree of alternation of a polymer, if the limiting degree of conversion can be determined. For example, when zinc reacts with polyvinyl chloride, cyclopropane rings are formed at a relatively high rate, and the reaction levels off at 86.5 per cent in agreement with the theoretical prediction.

\[
\begin{align*}
\text{Zn} & \quad \text{CH}_2\text{CH}_2\text{Cl} \\
& \quad \text{CH}_2\text{CH}_2\text{Cl} \\
& \quad \text{ZnCl}_2 \\
\end{align*}
\]

Zinc dechlorination of 1,2 vicinal units, if they are present, produces double bonds instead of rings, and the presence of these double bonds enhances considerably further dehydrochlorination.

If a polymer contains both structural units, dechlorination and dehydrochlorination will occur simultaneously, and the final degree of conversion would be meaningless. As mentioned above, highly syndiotactic polyvinyl chloride, although very likely of 1,3 alternate structure, on treatment with zinc, gives as well as cyclopropane rings appreciable amounts of double bonds. The origin of the latter could be found either in a rearrangement reaction or in a dehydrochlorination, which should be easier with syndiotactic
structures. A structural interpretation of the data becomes practically impossible.

Intramolecular reactions of functional groups are very often accompanied by cyclizations. In this event, such reaction should also obey Flory’s calculations, and the limited degrees of conversion would give indications concerning the internal structure of the polymer. Several examples of these cyclizations have been described in the literature. However, the percentage of reaction is always appreciably lower than foreseen (about 65 per cent maximum) on account of stereochemical restrictions which also play an appreciable role. These interfunctional reactions have however been used previously in order to obtain some information about sequence length and sequence distribution for some copolymers. Vinyl acetate–maleic anhydride copolymers should have an almost completely alternating structure on the basis of the corresponding copolymerization parameters. Indeed, after hydrolysis, the copolymer undergoes an internal lactonization in acid medium with formation of five- and six-membered rings (about 42 per cent lactones). Similarly, the extent of lactonization in hydrolysed vinyl acetate-methylacrylate copolymers has been examined from the point of view of sequence distribution, assuming a head-to-tail configuration and that reaction only occurs intramolecularly at intersequence junctions of vinyl alcohol–acrylic acid. Lactonization cannot be complete since a monomeric unit (acid or alcohol) flanked by two similar units is incapable of reaction. Furthermore, even in alternating structures, some functions become isolated. Allfrey and co-workers have shown that the fraction of the total unlaconiized acid can be expressed in terms of the copolymer composition and the alternating tendency \((1 - \frac{1}{2} f_2)\). The experimental results agree satisfactorily with the calculated values and, consequently, confirm the initial assumptions. These considerations were also used for demonstrating the formation of block polymers during some emulsion polymerization experiments. They are probably also valid for the lactonization of vinyl chloride–methyl methacrylate copolymers (carried out at 150°C with evolution of methyl chloride) provided that secondary reactions such as dehydrochlorination can be avoided.

Chemical structure has been often determined by oxidative cleavage reaction. The use of ozone as a tool in structure determination was most successful in the field of elastomers. It enables not only the determination of the relative importance of 1,2 and 1,4-addition, but also establishes the structure of emulsion-polymerized butadiene–methyl methacrylate-copolymers. By ozonolysis of a 1/1 copolymer and quantitative determination of the oxidation products, it was possible to demonstrate a very strong alternate structure: only 9-2 per cent succinic derivatives were isolated compared with more than 50 per cent of tricarboxylic acid.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_2 \quad \text{CH} = \text{CH} - \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \\
\text{COOMe} & \quad \text{CH}_3 \\
\text{HOOC} - \text{CH}_2 - \text{CH}_2 - \text{COOH} & \quad \text{CH}_3 \\
\text{HOOC} - \text{CH}_2 - \text{CH}_2 - \text{C} - \text{CH}_3 - \text{COOH} & \quad \text{COOMe}
\end{align*}
\]
ANALOGOUS POLYMERS

Another example of cleaving oxidation is given by the use of periodic acid on hydrolysed vinyl acetate–vinylidene carbonate copolymers. The comparison of the amount of periodic acid consumed with that of formic acid produced by oxidation is related to the number-average sequence lengths of vinylene glycol units. However, the oxidation products (malondialdehyde and hydroxymalondialdehyde) also consume periodic acid producing formic acid and carbon dioxide. On the other hand, polyvinyl alcohol itself is not insensitive to periodic acid on account of the presence of some 1,2 additions linkages. The lack of selectivity of the method, therefore, limits its validity for evaluating the sequence distribution, and necessitates that some correction be made.

These few examples show clearly the several restrictions and limitations imposed to the chemical methods for establishing a detailed polymer structure. On the other hand, as soon as this structure becomes more intricate or when several structures are present simultaneously, chemical methods become most important for the elucidation of chain composition. In this respect, the recent and excellent work of Schulz and Kern on polyacrolein constitutes the nicest example. The structure of polyacrolein varied according to the method of polymerization, and was essentially demonstrated on the basis of several polymer transformation reactions. Radical polymers consist mainly of very reactive side cyclic hemiacetal rings (structure a) whereas anionic and cationic polymers have only 9–15 per cent of aldehyde groups besides important unsaturated vinyl groups (structure b)

\[
\begin{align*}
\text{a} & : \quad -\text{CH}_2\text{CH}-\text{CH}_2\text{CH-CH} & \text{b} : \quad -\text{CH}_2\text{CH}-\text{CH-O-} \\
\text{O} & \quad \text{CH} & \text{HC-O} & \quad \text{CH=CH}_2 \\
\end{align*}
\]

ANALOGOUS CHEMICAL REACTIONS

The analogy between monofunctional polymeric reactions and reactions on homologous low molecular weight compounds has been recognized for many years; most “polymeranalog Umsetzungen” described by Staudinger were monofunctional and reversible reactions of high yield. Previous review have stressed the importance of the functionality of the reaction and of the structure of the polymer with respect to this analogy.

Sometimes the reaction proceeds quantitatively, e.g., the synthesis of poly(p-amino-polystyrene) via the Schmidt rearrangement of poly(p-acetylstyrene)

\[
\begin{align*}
\text{CH}_2\text{CH} & \quad \text{C}_6\text{H}_4 + \text{HN}_3 & \quad \text{C}_6\text{H}_4 - \text{H}_3\text{O}^+ \\
\text{CO} & \quad \text{NH} & \quad \text{NH}_2 \\
\text{CH}_3 & \quad \text{CO-CH}_3 & \quad \text{N}_2 \\
\end{align*}
\]

221
G. SMETS

Sometimes also reaction analogy data confirm conclusions concerning the internal structure of a polymer. Nakayama\(^{55}\) compared the rate of alkaline hydrolysis of radical and anionically polymerized maleimide with that of succimide and \(N\)-butyl-succimide. The data are summarized in Table 4.

**Table 4.** Alkaline hydrolysis of polymaleimide

\[
t^o = 25^\circ C \text{ (Imide) } = 5 \times 10^{-3}\text{mole l}^{-1} \text{ (NaOH) } = N/200
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>(k_2 \text{ (mole}^{-1} \text{ min}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)-butyl succimide</td>
<td>5.5</td>
</tr>
<tr>
<td>t-butoxide-polymerized maleimide</td>
<td>5.5</td>
</tr>
<tr>
<td>Succimide</td>
<td>0.45</td>
</tr>
<tr>
<td>Radical polymerized maleimide</td>
<td>0.0093</td>
</tr>
</tbody>
</table>

Anionically polymerized polymaleimide hydrolyses about 600 times faster than the radical polymer, and at the same rate as \(N\)-butyl succimide. These results strongly support an isomerization–propagation reaction through the imide-nitrogen, and the resulting structure was confirmed by complementary spectroscopic data. The reaction scheme can be represented as follows:

\[
\text{RO}^- + \text{CH} = \text{CH} \xrightarrow{\text{maleimide}} \text{RO}^- \text{CH} \xrightarrow{\text{CH}} \text{CO} \quad \text{RO}^- \text{CH} \xrightarrow{\text{NH}} \text{CO}
\]

The radical polymer

\[
\text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CO} \quad \text{CO} \quad \text{CO} \quad \text{CO} \quad \text{CO} \quad \text{NH} \quad \text{NH}
\]

has a holocarbon chain; in alkaline medium the imide groups become charged and exercise a strong electrostatic repulsion towards the attacking hydroxyl ions\(^{56}\)
ANALOGOUS POLYMERS

\[
\begin{align*}
-\text{CH} & -\text{CH} - \text{CH} - \text{CH} \\
\text{CO} & \quad \text{CO} \quad \text{CO} \quad \text{CO} \\
\quad & \quad \quad \quad \text{N} \quad \text{N}
\end{align*}
\]

Consequently, the rate of hydrolysis is very low compared to the low molecular weight homologues.

Nevertheless, even for monofunctional reactions, some caution is sometimes necessary in making comparisons between polymers and related model compounds. As an illustration of this point of view, two oxidation examples will be first considered: the hydroperoxydation of saturated hydrocarbon polymers and the oxidation of polythiols.

The relative rates of oxidation of polypropylene (A) and of polypropylene-2-\textit{d}_1 (B) have been compared very recently\textsuperscript{57}. The deuterated polymer shows not only a longer induction period, but also displays a considerably slower oxidation rate—the ratio \( k_A / k_B \) being 4.26 at 100°C. The tertiary carbon position is the site for initial oxidation attack and for the rate-controlling step in the further thermal oxidation. This is in agreement with the usual order of reactivity of hydrogen atoms in saturated hydrocarbons tertiary \( > \) secondary \( > \) primary and confirms previous data of Natta and co-workers\textsuperscript{58}.

Similarly, poly-\textit{p}-isopropylstyrene oxidizes very easily\textsuperscript{59}, and the rate of decomposition of the tertiary hydroperoxide is similar to that of cumene hydroperoxide. Polystyrene, however, oxidizes extremely slowly at 100°C, although the withdrawal of the \( \alpha \)-hydrogen would produce benzyl-type radicals. This high stability was attributed to either a loss resonance stabilization of radical due to steric hindrance which would prevent coplanarity, or to some shielding effects exercised by the phenyl groups\textsuperscript{60}.

The rate of oxidation of polymeric thiols compared to that of model substances is another example where the reaction analogy appears to fail. Overberger and co-workers examined the relative oxidizabilities in dimethylformamide of aliphatic and aromatic mercaptans; the data are summarized in Table 5.

Hydrolyzed polyvinyl thiol acetate is oxidized 9.4 times as fast as its model 2,4-pentanediithiol; the fact that any thiol of the polymer is flanked by two other thiol groups instead of one for the model could be at least partially responsible for the great rate difference.

At pH 10, polyvinyl-phenyl-thiol is oxidized 7.6 as fast as \( \text{p}-\text{thiocresol} \), but at a rate similar to that of its di(thiol-phenyl)pentane model. On account of the steric requirements of the phenyl groups, the approach of neighbouring groups is inhibited and the proximity effect, mentioned above, disappears.

Polymer reaction rates often differ significantly from the rate of their low molecular weight homologues when a macromolecule carrying a large number of ionic groups is involved in a reaction with a reagent of similar or opposite charge. Not only can the electrical potential of the polymeric chain vary with the degree of conversion, but also the overall shape of the molecule and, in consequence, the accessibility of the functions change. This variation of electrical potential explains the progressive decrease of
the experimental rate "constant" as the reaction proceeds in the alkaline hydrolysis of pectinic acid,\textsuperscript{62} polyacrylamide and polymethacrylamide\textsuperscript{63–65}. Only a few reactions of charged polymeric polyanion with a reagent of opposite charge have been reported: the reaction of partially ionized poly-4-vinylpyridine with bromoacetic acid\textsuperscript{66} which is favoured by the electrostatic attraction:

\begin{align*}
CH_2 &- CH - CH_2 - CH - CH_2 - \quad + \text{BrCH}_2 \text{-COO}^-\quad + \text{Br}^- \\
C_6H_4\text{NH} &+ C_5H_4\text{N} \\
\rightarrow CH_2 &- CH - CH_2 - CH - CH_2 - \quad + \text{C}_6H_4\text{NH}\quad + \text{C}_5H_4\text{N}^+ \\
&+ \text{CH}_2 \text{-COO}^- \quad + \text{H}_2\text{O} \\
C_6H_4\text{NH} &+ C_5H_4\text{N} \\
\end{align*}

and the catalysis of the hydrolysis of 3-nitro-4-acetoxybenzenesulphonate in the presence of partially ionized poly-4-vinylpyridine\textsuperscript{67}. This reaction passes through a maximum when 20 per cent of the polymer is ionized. Its mechanism can be written:

\begin{align*}
\text{CH}_2 &- \text{CH}_5 \quad \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{CH}_2 - \quad + \text{NO}_2 \quad \text{m} \quad \rightarrow \quad \text{CH}_2 &- \text{CH}_5 \quad \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{CH}_2 - \quad + \text{NO}_2 \quad \text{m} \\
\text{C}_6\text{H}_4\text{NH} &+ \text{C}_5\text{H}_4\text{N} \\
\text{OAc} \quad [p] \quad \rightarrow \quad \text{C}_6\text{H}_4\text{NH}^+ &+ \text{C}_5\text{H}_4\text{N} + \text{NO}_2 \quad \text{m} \\
&+ \text{H}_2\text{O} \\
\end{align*}
ANALOGOUS POLYMERS

These electrostatic effects on the reactivity of polions have been discussed in detail by Morawetz in a recent review to which the reader should refer.\(^{68}\)

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225
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