POLYMERIZATION AND COPOLYMERIZATION OF TRIOXANE

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POLYOXYMETHYLENE

Polyoxymethylene (POM) are formed by polycondensation (partially also by polyaddition) on evaporation of aqueous solutions of formaldehyde; paraformaldehyde has a degree of polymerization of up to \( \sim 100 \). The degree of polymerization of \( \alpha-, \beta- \) and \( \gamma \)-polyoxymethylene is not substantially higher.

Very high molecular-weight products can be obtained by anionic or cationic polymerization of monomeric formaldehyde with or without a diluent (\( \bar{P} \sim 100 \) to 100,000). Similar products can be obtained by a ring-opening polymerization of cyclic oligomers, especially trioxane.

H. Staudinger1, 2 and his school in the years between 1922 and 1932, had elucidated some of the principal concepts of the polymer chemistry using polyoxymethylene.

Polyoxymethylene having a degree of polymerization up to \( \bar{P} \sim 100 \) are undoubtedly linear; their thermal and chemical stability depends on the nature of the end groups. POM diols are unstable, POM diacetates are thermally stable, POM dimethyl ethers are, in addition, stable to alkali. For scientific purposes the thermal stability is measured3 without any additives under pure nitrogen at 190 to 200°C.

An obstacle to scientific and technical treatment of POM having a \( \bar{P} \sim 100 \)—the absence of suitable solvents—remained for a long time. It is to the merit of Alsop, Punderson and Leverett4 that they found appropriate solvents so that, at present, physico-chemical investigations are possible in certain phenols and in dimethylformamide.

SUBSEQUENT TRANSFORMATION OF UNSTABLE HEMIACETAL END GROUPS OF POM DIOLS

Staudinger studied transformations of POM diols having a \( \bar{P} \) up to \( \sim 100 \) which had been obtained from aqueous solutions of formaldehyde. Such transformations are difficult to carry out because the crystalline lattice is well ordered and because there is a rapid splitting-off of monomeric formaldehyde at the numerous hemiacetal groups. In a sample with a \( \bar{P} \sim 100 \) the initial rate of the decomposition reaction is 10 times higher than in a sample having a \( \bar{P} \sim 1000 \). Chemical conversions of the hemiacetal groups are much easier in the case of polymers (\( \bar{P} \sim 1000 \)) made from anhydrous formaldehyde than with polycondensates (\( \bar{P} \sim 100 \)) obtained from aqueous solutions, for the latter have a considerably higher degree of crystallinity. We can assume that the bulk of the end groups are located in the amorphous
regions of the polymer (25 per cent) as these break up the regularity of the lattice structure and hence are one of the origins of the amorphous fraction. Owing to this fact, the acetylation of the hemiacetal groups is possible in the solid state (in suspension) although it is not complete\(^5,\) \(^6\). Such experiments can be used to determine the portion of the end groups which are situated within the lattice and are, therefore, inaccessible.

**POLYMERIZATION OF TRIOXANE**

Pure trioxane displays the phenomenon of the “spontaneous” polymerization\(^7,\) \(^8\); this is very easily seen if the substance is repeatedly sublimed; at each operation a portion of POM stays behind as residue. This polymerization is caused by traces of monomeric formaldehyde. When the latter is removed (for instance with \(\text{Ag}_2\text{O}\)) or if trioxane is sublimed repeatedly in a high vacuum in an all-glass apparatus, it is completely stable. However, it can afterwards easily re-acquire the capability of undergoing “spontaneous” polymerization by the action of very small amounts of monomeric formaldehyde. We are still in the dark as to how to explain this spontaneous polymerization of trioxane brought about by the monomeric formaldehyde. The origin might be traced perhaps to orientation effects at the surface of trioxane crystals.

Trioxane undergoes cationic\(^9\) polymerization, for instance with \(\text{BF}_3\); we shall at present not discuss the topic of the cocatalyst\(^9,\) \(^10\). However, there is no error in the assumption that trace quantities of water \((10^{-3}\) mole per cent) which are removed only with the greatest difficulties, often play such a role. Protonic acids (e.g. \(\text{HClO}_4\)) are good initiators of the polymerization:

\[
\text{HO–CH}_2\text{O–CH}_2\text{O} \rightleftharpoons \text{H}_2\text{O} + \text{CH}_2\text{O}
\]

This type of initiation obviously gives rise to an unstable hemiacetal end group. At the resonance-stabilized C-cation of the cationic chain end which we therefore designate as the oxamethylene cation, there occurs an easy splitting-off of monomeric formaldehyde until an equilibrium concentration of formaldehyde is reached. This gives rise to an induction period during which there is no formation of POM, but in which every addition of trioxane ring and its opening is followed by the splitting-off of monomeric formaldehyde. At a certain concentration formaldehyde is added to the cation
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as quickly as it is split off and the polymerization proper of trioxan begins; this is betrayed by the appearance of insoluble POM.

If trioxane could be made absolutely free of water we should be able to produce “living” macrocations. As this is practically impossible, the smallest traces of water or of methylene glycol cause chain transfer:

\[
\begin{align*}
\text{CH}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{HO-CH}_2-\text{OH} \\
\text{HO-CH}_2-\text{O-CH}_2 & \rightarrow \text{HO-CH}_2-\text{OH} \\
\text{HO-CH}_2-\text{O-CH}_2 & \rightarrow \text{HO-CH}_2-\text{O-CH}_2-\text{O} \\
\text{HO-CH}_2-\text{O-CH}_2 & \rightarrow \text{HO-CH}_2-\text{O-CH}_2-\text{O} + \text{H}^+
\end{align*}
\]

Nevertheless, degrees of polymerization exceeding \(2 \times 10^4\) can be achieved\(^{11, 12}\) by polymerizing high-purity trioxane.

The reaction scheme as above should also be examined from a different viewpoint, namely from that of the reactivity and stability of the respective cations. Despite the stabilization of the oxamethylene cation by resonance it seems right to assume that the cyclic oxonium cation is more stable; this is evidenced already by the high concentration of the monomeric trioxane which obviously adds immediately to a methylene cation in the process of its formation. If this is so, then molecules of ether should also add to such cations. This is actually the case, as is shown by a certain retardation which can result in inhibition of the polymerization in diethyl ether and similar solvents\(^{15, 20}\). It takes place because the oxonium ion so formed cannot eliminate the ethyl cation which is too rich in energy and not stabilized by resonance; the only possible decomposition is the unprofitable reverse reaction to form the oxamethylene cation:

\[
\begin{align*}
\text{HO-CH}_2-\text{O-CH}_2-\text{O} & \rightleftharpoons \text{HO-CH}_2-\text{O-CH}_2-\text{O} + \text{CH}_2 \\
\text{HO-CH}_2-\text{O-CH}_2-\text{O} & \rightarrow \text{HO-CH}_2-\text{O-CH}_2-\text{O} + \text{H}_3\text{C}^+ \\
\text{HO-CH}_2-\text{O-CH}_2-\text{O} & \rightarrow \text{HO-CH}_2-\text{O-CH}_2-\text{O} + \text{H}_3\text{C}^+
\end{align*}
\]

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Monomeric formaldehyde has the peculiar capability of undergoing cationic polymerization\textsuperscript{13, 14} in ether (and even in acetone). We must therefore assume that formaldehyde can eliminate ether molecules from the oxonium cations at chain ends.

**CHAIN TRANSFER REACTIONS WITH LOW-MOLECULAR-WEIGHT SUBSTANCES**

**With formals, especially with dimethyl formal**

The oxamethylene cation of the growing chain can form oxonium ions not only with trioxane, but also with other formals and acetals, \textit{e.g.} with dimethyl formal\textsuperscript{15} (Table I). In contrast to the oxonium ion with diethyl ether, such an oxonium ion is easy to split since there can be formed an oxamethylene cation which is similar to the normal growing chain end, is stabilized by resonance and capable of propagation:

\[
\begin{array}{c}
\text{\textbullet\text{-O-CH\textsubscript{2}-O-CH\textsubscript{2} + O-CH\textsubscript{2}-O-CH\textsubscript{3}}} \\
\text{CH\textsubscript{3}}
\end{array}
\]

\[
\begin{array}{c}
\text{\textbullet\text{-O-CH\textsubscript{2}-O-CH\textsubscript{2}-O + H\textsubscript{3}C-O-CH\textsubscript{2}}} \\
\text{CH\textsubscript{3}}
\end{array}
\]

\[
\text{H\textsubscript{3}C-O-CH\textsubscript{2} + trioxan \rightarrow H\textsubscript{5}C-O-CH\textsubscript{2} \ldots \text{O-CH\textsubscript{2}}}
\]

The macromolecule formed is terminated by a methoxyl group and the new growing chain begins with a methoxyl group. This produces macromolecules with two stable methoxyl end groups. Working with a system as free of water as possible yields polyoxymethylene dimethyl ether having a degree of polymerization of \(\sim 500\) and more\textsuperscript{15}. These products which are stable to both heat and alkali served in a calibration of the viscometric method for determination of the molecular weights of POM in dimethylformamide\textsuperscript{16}. When working with such molecular weights we have to bear in mind that our polymers were fractionated; in case of unfractionated samples we, therefore, assume a coefficient of heterogeneity \(U \sim 2\), as has been also assumed by others\textsuperscript{16a}.

**With cationically cleavable ethers, with esters and anhydrides**

It is easy to see that not only acetals, but also low-molecular-weight ethers and esters can act as chain-transfer agents provided that the oxonium ion formed is capable not only of splitting off the oxamethylene cation originally added—this in itself produces no change—but also is capable of eliminating one of the two remaining ligands by a cationic mechanism, forming another resonance stabilized cation; this is what happens in the case
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of diallyl ether or methyl formate or acetic anhydride and, of course, in the analogous compounds\(^\text{15}\). The cations eliminated from the oxonium ions and stabilized by resonance are then the allyl cation, the formyl and the acetyl cation. This chain transfer can give rise to stable ether end groups (allyl ether or methyl ether) or to ester end groups which are only thermally stable (not stable to alcalis). The new initiating cations also form end groups of different stabilities.

<table>
<thead>
<tr>
<th>Examples</th>
<th>Chain transfer constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formals (Acetals)</td>
<td>CH(_3)O—CH(_2)—O—CH(_3)</td>
</tr>
<tr>
<td>Ethers</td>
<td>(CH(_2)=CH—CH(_2))_2O</td>
</tr>
<tr>
<td>Esters</td>
<td>CH(_3)O—C—O</td>
</tr>
<tr>
<td>Anhydrides</td>
<td>(CH(_3)=C—)(_2)O</td>
</tr>
<tr>
<td>Halogenated substances</td>
<td>CCl(_4)</td>
</tr>
<tr>
<td>Water</td>
<td>H(_2)O or HO—CH(_2)—OH</td>
</tr>
</tbody>
</table>

Finally it must not pass unnoticed that each available water molecule produces two unstable end groups through a chain transfer mechanism and that owing to its very high chain transfer constant water is unusually active even at very low concentrations. It is therefore necessary to dry the monomeric trioxane very painstakingly, especially if one wants to produce stable end groups by chain transfer.

CHAIN TRANSFER REACTIONS WITH MACROMOLECULAR SUBSTANCES

It follows easily from the above that macromolecular substances must also act as chain transfer agents provided they contain acetal, cleavable ether or ester groups. Depending on the position of the oxygen atom being attacked by the growing chain, these chain transfer reactions yield either linear block copolymers, grafted copolymers or crosslinked products.

**Chain transfer to oxygen atoms of the main chain of polymers which can undergo electrophilic attack; formation of block copolymers**

For example, the cationic polymerization of trioxane can be chain transferred with polyglycol formal (polydioxolane) which is also produced by cationic polymerization:
This reaction is in fact a copolymerization and can be designated as such. It yields at first linear macromolecules having the structure of a block copolymer. With progressing reaction, however, the blocks of polyglycol formal are attacked repeatedly by the growing polyoxymethylene cations and thus broken down. Finally, the polyglycol formal originally present is disintegrated to a large extent to separate glycol formal building units connected on either side to blocks of polyoxymethylene\cite{17}, \cite{18}.

We can also expect to find such chain transfer reactions with respect to polyoxymethylene chains\cite{18}; however, this has not been proved with final validity. It would mean that in the course of a cationic homopolymerization of trioxane or of formaldehyde there is chain transfer to chains of polyoxymethylene already formed.

All this seems to be reasonable and a matter of course; however, we must not overlook the complication, which is not altogether clear, imposed by the heterogeneous reaction. We do not know much about what happens inside the polymer particles already formed and suspended in the reaction medium, nor how deep the monomeric trioxan or the monomeric formaldehyde—which is present in an equilibrium concentration—can penetrate into these particles and disrupt the crystal structure in order to react with the dormant (starving) cations. It appears as if these problems were similar to those of a popcorn polymerization. Nor could a comparison with the doubly heterogeneous polymerization of olefins with solid catalyst such as TiCl\(_3\)/AlR\(_3\) forming a solid and crystalline polymer be altogether dismissed. The situation in a trioxane polymerization is somewhat simpler since we need not take into account a heterogeneous catalyst.

The chain transfer with polyesters such as polyethylene terephthalate proceeds in an analogous way\cite{18}:

A substantial advantage of chain transfer with polymers undoubtedly consists in the fact that the molecular size is not as reduced as in the case of the
transfers with a low molecular-weight substance, e.g., with dimethyl formal or with methyl benzoate, the low molecular-weight analogues of polyglycol formal and polyethylene terephthalate. These low molecular-weight chain transfer agents produce only end groups while polymeric chain transfer agents incorporate segments of themselves into the chain. This is also a reason for calling such a process a copolymerization although, in fact, it is a chain transfer. The effect of chain transfer with polymers resembles copolymerization with cyclic compounds.

**Chain transfer to oxygen atoms of the side chains of polymers which can undergo electrophilic attack; formation of grafted copolymers**

Examples of such polymeric chain transfer agents are polyvinyl acetate and polyacrylates:

\[ -\text{CH}_2-\text{CH}- \]
\[ -\text{OCH}_2-\text{OCH}_2 + O \rightarrow \]
\[ \text{O=C-CH}_3 \]
\[ \ldots-\text{CH}_2-\text{CH}- \]
\[ \ldots-\text{OCH}_2-\text{OCH}_2-O \] + \[ \text{O=C-CH}_3 \]
\[ \text{O=C-CH}_3 + \text{trioxan} \rightarrow \text{O=C-CH}_2-\text{OCH}_2-\text{OCH}_2 \]
\[ \text{CH}_3 \]
\[ -\text{OCH}_2-\text{OCH}_2 + -\text{CH}_2-\text{CH}- \rightarrow \]
\[ \text{C=O} \]
\[ \text{OCH}_3 \]
The polymers produced are thermally stable, as could be expected but have not been sufficiently studied so far.

**Chain transfer to acetals of polyvinyl alcohol**

In agreement with expectation the products are crosslinked. What actually happens is a true copolymerization with six-membered rings in the main chain whose acetal groups are attacked and opened:

This shows that the chain transfer to polymers in the cationic polymerization of trioxane opens the way to truly new prospects; it leads to true copolymers obtainable otherwise only through copolymerization. This point is made especially clear in the following discussion of the copolymerization.

**COPOLYMERIZATION OF TRIOXANE**

Two points are of importance when discussing the choice of comonomers for trioxane. First, it appears expedient to choose such components which can undergo cationic polymerization. The following substances would suitably satisfy this criterion:

(i) aldehydes, because of the polar limiting structure of the carbonyl group;

(ii) oxacyclic compounds such as cyclic acetals, cyclic ethers, lactones and cyclic anhydrides. Knowledge of the chain transfer propensity may help in the selection;

(a) Cyclic acetals

\[
\begin{align*}
\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{O} & \quad \text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{O} \\
\text{CH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{O} & \quad \text{CH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{CH}_2 & \quad \text{CH}_2\text{CH}_2 \\
\text{O} & \quad \text{C}_6\text{H}_5\text{CH} \\
\text{CH}_2 & \quad \text{O} \\
\text{Dioxolan} & \quad \text{4-Phenyl-1,3-dioxane} \\
\end{align*}
\]
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(b) Cyclic ethers

<table>
<thead>
<tr>
<th>Ethylene oxide</th>
<th>Styrene oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene oxide</td>
<td>3,3-Bis(chloromethyl)oxacyclobutane</td>
</tr>
</tbody>
</table>

(c) Lactones and cyclic esters

| β-Propiolactone | 2,5-Dioxacyclopentanone |
| γ-Butyrolactone | | |

(iii) vinyl derivatives such as styrene, vinyl ethers or indene.

The second principle for the selection of the comonomers follows a definite aim, namely the formation of thermally stable and, if possible, alkali-resistant polyoxymethylene. The point is to build a polymer chain with such a varied composition that the unzipping reaction of the polyacetel chain with hemiacetal end groups, which would otherwise result in complete depolymerization, is prevented or proceeds only partially. It is easy to see that the second objective cannot be achieved with a carbonyl compound which undergoes cationic polymerization because that would also produce a polyacetel chain which, owing to the presence of hemiacetal groups at the ends, would decompose thermally and chemically. Hence, although a thorough investigation of the copolymerization of trioxane with aldehydes or ketones would be attractive we made no attempts so far in that direction.

What can be achieved by copolymerization of trioxane with cyclic compounds as regards the stability of the polymer will be briefly shown using the example of the copolymerization with glycol formal (dioxolane):

\[
\begin{align*}
\text{HO} & \quad \text{-X-} \quad \text{-X-} \quad \text{-X-} \quad \text{-X-} \quad \text{-X-} \quad \text{-OH} \\
\text{Unstable} & \quad \text{Thermally stable and alkali-resistant} \quad \text{Unstable}
\end{align*}
\]

The electrophilic oxamethylene cation can be expected to add to dioxolane with the same ease as to trioxane; the oxonium so formed can either split back into the original compounds or open the five-membered ring. Ring opening occurs more easily at the formal linkage because this also generates a resonance-stabilized chain end. Also it does not require a higher energy expenditure than the opening of the oxonium ion of a terminal trioxane ring, although this is possible in two ways. It is of special importance to note that in this way an oxamethylene cation is generated the reactivity of which towards trioxan resembles that of the product of opening of the oxonium
ring of the trioxane unit. This fulfills the prerequisites of a favourably copolymerization of trioxane and dioxolane so that an appropriate choice of concentration of the two comonomers can determine the structure of the copolymer chains. A preferential formation of blocks of the dioxolane units is not to be expected, except perhaps at the beginning of the reaction during the induction period in which monomeric formaldehyde is liberated.

The effect of the copolymerization is easy to trace. The separate glycol building units (X), connected at both sides to polyoxymethylene chains (\(-\varepsilon\varepsilon\varepsilon\varepsilon\)), break up the polyacetals chains. They also affect thermal stability and alkali-resistance of the copolymer after the relatively short unstable terminal sequences, each having a hemiacetal end group, have been destroyed by thermal or alkaline treatment. This partial degradation stops because the glycol end groups are of the ether type, a prerequisite for the stable polyoxymethylene which had been discovered by Staudinger more than 30 years ago.

The results of such a copolymerization\textsuperscript{19} are shown in Table 2 which also indicates the monomer reactivity ratios; they indicate that we are dealing with an almost ideal copolymerization.

\[
\text{Table 2. Copolymerization of trioxane (M}_1\text{) with glycol formal (M}_2\text{) in nitrobenzene with CH}_3\text{C}^+\text{ClO}_4^-\text{ at 35°C}\\
\]

<table>
<thead>
<tr>
<th>Monomer feed</th>
<th>Portion of thermally stable copolymer (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1</td>
<td>93</td>
</tr>
<tr>
<td>6 : 1</td>
<td>83</td>
</tr>
</tbody>
</table>

Monomer reactivity ratios: \( r_1 = 1.36 \pm 0.03; r_2 = 0.47 \pm 0.15 \)

Besides dioxolane, other cyclic formals\textsuperscript{19, 20} have been studied and found to offer similar advantageous possibilities.

Not all of the cyclic ethers undergo copolymerization with trioxane. This is related to the difficulty of opening the ether rings of the cyclic oxonium ions analogous to the chain transfer with open-chain ethers. The strain of the ethylene oxide ring and of other epoxy rings makes such an opening possible although this cannot give rise to a resonance-stabilized methylene cation. The cation formed is certainly very reactive and can, in principle, add to both monomers; the copolymerization can therefore take place:

\[
\begin{align*}
\text{OCH}_2\text{OCH}_2\text{OCH}_2^+ + \text{CH}_2 \text{OCH}_2\text{OCH}_2\text{OCH}_2^+ & \rightarrow \\
\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2^+ & + \text{CH}_2 \text{OCH}_2\text{OCH}_2\text{OCH}_2^+ + \text{Trioxane} \\
\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2^+ & + \text{Trioxane} \\
\end{align*}
\]
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Certain complications can be expected at the start of the reaction; the prepolymerization of ethylene oxide\textsuperscript{17} actually observed could result in the formation of sequences of polyethylene oxide whose effect on the stability of the copolymers would be much less than that of an equivalent number of separate glycol units. There are reasons to suppose that homopolymerization of ethylene oxide proceeds—if at all—only in the initial stage of the reaction, \( i.e. \), during the induction period in which the concentration of formaldehyde formed has not yet reached its equilibrium value. Considering the high reactivity of monomeric formaldehyde towards cations—which is manifested by the fact that its polymerization proceeds cationically even in diethyl ether as solvent—it is quite possible that the monomeric formaldehyde can influence the decomposition of such oxonium ions

\[
\begin{array}{c}
\text{CH}_2 \\
\text{O--CH}_2\text{--CH}_2\text{--O} \\
\text{CH}_2
\end{array}
\]

in spite of the low reactivity of the ether oxonium ions. It is, however, quite possible that the terminal \( \text{CH}_2 \) cation of the ethylene oxide is more reactive toward the monomeric formaldehyde than toward ethylene oxide so that the very low concentration of the formaldehyde which is established soon after the beginning of the polymerization suffices to prevent the formation of homopolymeric sequences of ethylene oxide units. In the case of the “binary” copolymerization of trioxane one has to consider not two but three monomers which are involved in a terpolymerization, namely trioxane ethylene oxide \( i.e. \) formaldehyde.

It should be mentioned that in the light of the finding of Weissemel and Hermann\textsuperscript{17}, prepolymer of ethylene oxide and trioxane are incorporated by copolymerizing chain transfer during the polymerization of the trioxane in the same manner described for the case of polymeric dioxolane. Let us state only that the derivatives of ethylene oxide and of oxacyclobutane and, undoubtedly oxacyclobutane itself also copolymerize with trioxane; higher-membered cyclic ethers, however, copolymerize with much more difficulty and retard reaction.

Other interesting comonomers for the trioxane are lactones\textsuperscript{19, 20}, especially \( \beta \)-propiolactone\textsuperscript{19}. It is readily understood that this four-membered ring copolymerizes easily through a mechanism similar to that previously formulated for the chain transfer with esters:

\[
\begin{array}{c}
\text{OCH}_2\text{--O--CH}_2 \quad \text{O--CO} \\
\text{CH}_2\text{--CH}_2 \\
\end{array}
\rightarrow
\begin{array}{c}
\text{OCH}_2\text{--OCH}_2\text{--O--CH}_2\text{--CH}_2\text{--C}^+ \\
\text{O} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{OCH}_2\text{--OCH}_2\text{--O--CH}_2\text{--CH}_2\text{--C--OCH}_2\text{--OCH}_2\text{--O} \\
\end{array}
\]
Such copolymers are thermally quite stable, but display the same weakness of the ester groups towards alkalies observed for polyoxymethylenes having acetyl end groups. It is also clear that higher lactones can easily copolymerize with trioxane since the stabilization by resonance of the terminal acyl cation makes possible the opening of a ring which is free of ring strain.

We shall not discuss cyclic anhydrides\textsuperscript{20} in detail. We shall also only touch upon the copolymerization of trioxane with vinyl derivatives\textsuperscript{12, 21, 22} which has been studied in detail. The incorporation of styrene into the polyoxymethylene chain has been elucidated\textsuperscript{23}. The attack of the oxamethylene cation takes place at the $\beta$-carbon of the styrene molecule:

$$
\begin{aligned}
\text{O--CH}_2\text{--O--CH}_2\text{--CH}_2\text{--CH} & \quad \text{O--CH}_2\text{--O--CH}_2\text{--CH}_2\text{--CH} \\
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5
\end{aligned}
$$

Cleavage of this copolymer under acidic conditions yielded 1-phenyl-1,3-propanediol, $\text{HO--CH}_2\text{--CH}_2\text{--CH--OH}$, which reacted further with $\text{C}_6\text{H}_5$ formaldehyde and was identified as 4-phenyl-1,3-dioxane,

$$
\begin{aligned}
\text{CH}_2\text{--CH}_2 & \\
\text{C}_6\text{H}_5\text{--CH} & \quad \text{O} \\
\text{O--CH}_2 & 
\end{aligned}
$$

As a result of these experiments we know at present that both the radical, the anionic and the cationic attack on the monomeric styrene always takes place at the same carbon atom. This phenomenon could be understood as a mesomeric elasticity of the phenyl nucleus.

Experiments involving numerous vinyl derivatives\textsuperscript{12, 21} have yielded thermally stable copolymers but, even in favourable cases such as in the case of styrene, the products were only of comparatively low molecular weight.

**CHAIN TRANSFER THROUGH HYDRIDE SHIFT**

The active species are of greatest importance when studying a polymerization reaction. They are not only the intermediates during chain growth which proceeds in most cases regularly and is therefore not very interesting but also, due to their high reactivity, we must expect them to be involved in side reactions which can affect the reaction product.

This can be easily seen in the case of the radical polymerization of vinyl derivatives. The growing macroradical which is often—but by no means
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always—resonance-stabilized can undergo recombination or disproportionation. It can also be transferred to monomer, to solvent, to impurities or to the polymer already formed. It can also be involved in an intramolecular chain transfer and produce short-chain branching. All of this affects the structure of the polymer (for instance by branching or by the allyl shift), affects the end groups and finally the distribution of the molecular weights.

In the case of ionic polymerizations side reactions comparable with the above have been observed, especially hydride shifts or proton migrations and, as a result, changes in the structure of the chains have been observed.

In this way Kennedy\textsuperscript{24} has found that cationic polymerization of 3-methylbutene-1 at $< -130^\circ C$ yielded a chain structure through the hydride shift at the cationically growing chain end which differed from the expected structure previously obtained with different catalysts. He proved that this is due to the 1,3 addition instead of the usual 1,2 addition:

\[
\begin{align*}
\text{CH}_2=\text{C} & \quad \text{CH} \\
\text{CH} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{Ziegler catalyst} \\
\text{H}_3\text{C} & \quad \text{AlCl}_3 \\
\text{130 C} & \quad \text{CH}_2=\text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

It had been noted as early as four years ago that the cationic polymerization of pure trioxan in solution can yield up to 60 per cent heat-stable and alkali-resistant polymer.\textsuperscript{22} At first we considered it feasible that this was due to an impurity contained in the solvent or in the monomer. However, two years ago it was discovered that a side reaction takes place at the growing chain end which yields stable end groups\textsuperscript{12, 25}. The same conclusion has been reached by Weissermel and Hermann\textsuperscript{26} on the basis of similar observations. Similar observations were made also in Brno in the institute of Professor Vesely\textsuperscript{27} without, however, being further considered or explained. There is one point about which the scientists of Hoechst and Mainz are unanimous, namely that a hydride shift must take place at the cationic chain end, since the observed and quantitatively determined methoxyl end groups cannot be explained in any other way, considering the high purity of the starting material.

There are two reactive cationic chain ends which can be responsible for the shift, namely the oxamethylene cation and the oxonium ion which still contains an intact trioxane ring at its chain end. The methylene cation is undoubtedly more reactive than the oxonium ion although it is resonance-stabilized; to ascertain this fact we have only to remember the stability of the oxonium ion which is formed through the addition of diethyl ether to the growing chain and which is, after all, responsible for the inhibition of
the polymerization occurring in ether. Both cations can in principle submit to the hydride shift:

\[
\begin{align*}
\text{OCH}_2\text{OCH}_2^+ & \rightarrow \text{OCH}_2\text{OCH} + \text{CH}_3^+ \\
\text{or} \quad \text{OCH}_2\text{OCH}_2^+ & \rightarrow \text{OCH}_2 + \text{OC}^+\text{OCH}_3 \\
\text{Methyl formate} & \quad \text{(chain transfer agent)} \\
\text{or} \quad \text{OCH}_2\text{OCH}_2^+ & \rightarrow \text{OCH} + \text{OC}^+\text{OCH}_3 \\
\text{Trioxanyl cation} & \\
\end{align*}
\]

We are inclined to attribute the greater importance to the oxonium ions because of their greater stability and longer life. It is, however, quite possible that the terminal oxamethylene cation is at the origin of the hydride shift because of its higher reactivity.

The difficulty involved in the observation of the hydride shift lies in the fact that it results only in the formation of end groups of a special type and not of chains displaying structural isomerism as in the case of the polymerization of 3-methylbutene-1.
POLYMERIZATION AND COPOLYMERIZATION OF TRIOXAN

POLYOXYMETHYLENES BRANCHED BY CHAIN TRANSFER

Reactions resembling those which produce stable end groups by a chain transferring hydride shift can produce polyoxyethylene chains branched by chain transfer. One should not dismiss such chain transfer as being impossible. The crystalline polymer particles which separate out of the reaction medium certainly contain oxamethylene cations inside the particle which, due to the shortage of monomeric trioxane, can attack methylene groups of the polyoxyethylene chains. As in the case of the trioxanyl cation a C-...ation belonging to a polyoxyethylene chain could add trioxane and so form a lateral branch.

\[
\begin{align*}
\text{CH}_2\text{O} \quad \text{CH}_2\text{O} \quad \text{CH}_2\text{O} \\
\text{H}_3\text{C} \quad \text{O} \quad \text{CH}_2\text{O} \\
\text{O} \quad \text{CH}_2\text{O} \quad \text{CH}_2\text{O} \quad \text{CH}_2
\end{align*}
\]

Of course, this hypothesis would have to be proved first. If it were true, one of the basic assumptions of polyoxyethylene chemistry, namely the assumption of the linear structure of the molecular chains, would prove false. Polyoxyethylene produced by cationic polymerization could display the same complications due to branching as most of the polymers studied so far.

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