SOME RECENT RESULTS OF END GROUP ANALYSIS BY DYE TECHNIQUES

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INTRODUCTION

The extreme ends of a polymer chain often have functional groups differing in composition from the main chain as such; these are called end groups. It is a challenge to chemists and physicists to identify and measure these end groups since they constitute a very small fraction of the macromolecule. Recent advances in functional group analysis are increasingly being pressed into service to do this delicate job and some degree of success has recently been achieved. Some applications of physical and chemical methods can be cited herein, for example, the determination of unsaturation by Entwistle, sulphide end groups by Rosenthal et al., hydroxyl end groups in polystyrene by Evans, alkoxy and fluorine groups by Bawn et al. and carboxyl in polytetrafluoroethylene by Bro and Sperati. But the usual chemical methods become increasingly insensitive and very often impractical with increasing molecular weight of polymer. The physical methods and tracer techniques also have their limitations.

Recently, we have developed two simple and rapid methods of detection and estimation of a few types of end groups based on dye-polymer interaction; these methods are called the “dye-partition technique” and “dye-interaction technique” respectively. These techniques are sufficiently sensitive for the characterization of end groups in vinyl polymers of high molecular weight. The two dye techniques are often complementary to each other and, when employed with the same polymer, yield much additional information. We report here a survey of our results of end group analysis obtained by using these dye technique.

IMPORTANCE OF END GROUP ANALYSIS

Information about the end group content not only adds to our knowledge of the structure of the polymer molecule, but it opens up the possibility of identifying the initiating species and this in its turn provides a clearer insight into the mechanism of initiation.

Secondly, the occurrence of vinyl or related polymerization is now an established method for a simple experimental demonstration showing the presence of transient free radical intermediates generated by thermal or photolytic dissociation of certain compounds, by electron transfer reactions in redox systems or by radical displacement reactions. The characterization of these radicals trapped as polymer end groups provides strong and direct evidence as to the nature and identity of the initiating radicals vis-à-vis the chemistry of free radicals. The end group content also throws light on the nature of the termination process.
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PRINCIPLE OF DYE-TECHNIQUES

Dye partition test

The principle is as follows: if a benzene or chloroform solution of a polymer contains say, an anionic end group, and is shaken with an aqueous solution of a cationic dye, the dye goes into the benzene or chloroform layer:

<table>
<thead>
<tr>
<th>Aqueous layer: ---</th>
<th>Dye +</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform layer: ( \text{---- COO}^- )</td>
<td>Na⁺</td>
<td></td>
</tr>
</tbody>
</table>

Coloration in the chloroform layer is an indication of the existence of ionic end groups in the polymer. By using suitable dyes, depending on the pH, this test can detect all kinds of ionic end groups in polymers.

Dye interaction technique

Solutions of a number of basic or acid dyes in aqueous buffer solutions of suitable pH when extracted with benzene, toluene or similar solvents yield organo-extracts, presumably of the “dye base” or: the “dye acid”. Acid dyes extracted at suitable acid pH yield benzene extracts which change colour in the presence of traces of a base (in benzene); basic dyes do the opposite. The same test is also applicable to polymers having acidic (anionic) and basic (cationic) end groups. The dye interaction method differs from the dye partition method in that the former is carried out in a homogeneous medium (usually benzene). Carboxyl, hydroxyl, sulphate, sulphonate, amino and halogen end groups have been identified by this method.

RESULTS

Most of our work has been carried out with methyl methacrylate in aqueous media using a variety of water-soluble initiators.

Initiation by hydrogen peroxide as oxidant

Fenton’s reagent (Fe²⁺ –H₂O₂) is a prolific source of hydroxyl radicals and has long been used to initiate aqueous vinyl polymerization. By the application of dye interaction techniques, all the polymers have been found to contain hydroxyl end groups (Table 1). Hydroxyl end groups have also been detected in all the methylethacrylate polymers obtained by aqueous photo-initiation with hydrogen peroxide. This is in agreement with the observation of Dainton⁸, who qualitatively detected OH end groups by infrared spectroscopy in such polymers. An average of 1 to 1.5 hydroxyl end groups⁹ per polymer chain has been obtained with Fe²⁺ –H₂O₂, or H₂O₂ in UV radiation, whereas for styrene polymerization using the same initiator (Fe²⁺ –H₂O₂), Evans⁸ obtained two OH groups per chain. It thus appears that in MMA polymerization, termination takes place mainly by disproportionation, at least in the concentration range of the initiator components used.
RESULTS OF END GROUP ANALYSIS

Table 1. Initiation by hydrogen peroxide as oxidant

<table>
<thead>
<tr>
<th>Initiating system</th>
<th>Monomer</th>
<th>Technique used</th>
<th>End group surmised</th>
<th>End group detected</th>
<th>No. of end-groups per chain</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂ (hy) Aq.</td>
<td>—</td>
<td>IR</td>
<td>OH</td>
<td>OH</td>
<td>—</td>
<td>(8)</td>
</tr>
<tr>
<td>H₂O₂ (hy) Aq. or (H₂O₂ + Fe²⁺)</td>
<td>MMA</td>
<td>Dye technique</td>
<td>OH</td>
<td>OH</td>
<td>1-0-1-5</td>
<td>(9)</td>
</tr>
<tr>
<td>Fe²⁺—H₂O₂ Aq.</td>
<td>Styrene</td>
<td>Chemical</td>
<td>OH</td>
<td>OH</td>
<td>2</td>
<td>(3)</td>
</tr>
<tr>
<td>FeCl₃—H₂O₂</td>
<td>MMA</td>
<td>Dye technique</td>
<td>OH</td>
<td>OH</td>
<td>2</td>
<td>(9)</td>
</tr>
</tbody>
</table>

Initiation by persulphate as oxidant

As regards initiation by persulphate alone, the initiating species are generally supposed to be SO₄⁻ radicals as evidenced by end group analysis by tracer technique¹⁰. End group analysis by dye techniques shows the presence of both SO₄⁻ and OH radicals in persulphate initiated polymer (Table 2).

\[
\text{S}_2\text{O}_8 \rightarrow 2\dot{\text{SO}}_4^- \quad (1)
\]

\[
\dot{\text{SO}}_4^- + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \dot{\text{OH}} \quad (2)
\]

The proportion of sulphate end groups in polymers is highly dependent on the pH of the polymerization medium; it increases with the alkalinity of the medium and sharply decreases under acid conditions. It appears that \(\dot{\text{SO}}_4^-\) radicals react very fast with water under acid conditions \((\dot{\text{SO}}_4^- + \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{SO}_4 + \dot{\text{OH}})\).

Persulphates in redox combination with other reducing sulphoxy compounds \((\text{NaH}_2\text{SO}_3, \text{Na}_2\text{SO}_3, \text{Na}_2\text{S}_2\text{O}_3, \text{Na}_2\text{S}_2\text{O}_4, \text{Na}_2\text{S}_2\text{O}_5)\), sodium sulphide, hydroxylamine, hydrazine, transitional metal ions such Ag⁺, Fe²⁺, Cu²⁺ etc. have been used as polymerization initiators¹², ¹⁴, ¹⁵ and the end groups present in such polymers have been extensively studied by us using dye techniques¹⁷, and, in some cases, by others using tracer techniques¹², ¹⁴ (Table 2).

Poly(methylethacrylate) samples obtained by aqueous redox initiation with persulphate in conjunction with reducing sulphoxy compounds are found by dye techniques to contain both hydrolysable sulphate end groups and nonhydrolysable sulphonate end groups (Table 2). It is relevant to point out that all reducing compounds, with the exception of thiosulphate, have also been found to be capable of initiating aqueous polymerization of methyl methacrylate by themselves and the sulphoxy end groups incorporated in the polymers have been found to be non-hydrolysable in all cases. It may, therefore, be concluded that in redox initiation with persulphate and reducing sulphoxy compounds, the hydrolysable sulphoxy end groups are sulphate end groups evidently derived from persulphate molecules and the non-hydrolysable sulphoxy end groups are sulphonate end groups evidently

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derived from the activator molecules. Reports in the literature\(^\text{12, 16, 17}\) suggest that, in redox initiation involving persulphate and a reducing sulphoxy compounds incorporation of sulphoxy end groups in the polymer from both the redox components is possible and this is further confirmed by our results.

**Table 2. Initiation by persulphate as oxidant**

<table>
<thead>
<tr>
<th>Initiating system</th>
<th>Monomer</th>
<th>Technique used</th>
<th>End group survived</th>
<th>End group detected</th>
<th>No. of end-groups per chain</th>
<th>Remarks &amp; Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{S}_2\text{O}_8^{2-}) or (\text{Fe}^{3+} + \text{S}_2\text{O}_8^{2-})</td>
<td>Styrene</td>
<td>Tracer</td>
<td>Sulphate</td>
<td>Sulphate</td>
<td>1-2-3-1 or 0-9-2-8</td>
<td>(10)</td>
</tr>
<tr>
<td>(\text{S}_2\text{O}_8^{2-})</td>
<td>Tetra-fluoro-ethylene</td>
<td>Tracer</td>
<td>Sulphate</td>
<td>No sulphate</td>
<td>Nil</td>
<td>(12)</td>
</tr>
<tr>
<td>(\text{S}_2\text{O}_8^{2-})</td>
<td>Tetra-fluoro-ethylene</td>
<td>IR</td>
<td>OH</td>
<td>COOH</td>
<td>—</td>
<td>(5)</td>
</tr>
<tr>
<td>(\text{S}_2\text{O}_8^{2-})</td>
<td>Alkyl acetate</td>
<td>Chemical</td>
<td>Sulphate</td>
<td>Sulphate</td>
<td>0-75</td>
<td>(13)</td>
</tr>
<tr>
<td>(\text{S}_2\text{O}_8^{2-})</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>Sulphate and OH</td>
<td>Sulphate</td>
<td>1-5-2-5</td>
<td>(11)</td>
</tr>
<tr>
<td>(\text{S}_2\text{O}_8^{2-} + \text{HSO}_4^{-})</td>
<td>Tetra-fluoro-ethylene</td>
<td>Tracer</td>
<td>Sulphate and sulphonate</td>
<td>Sulphate and OH</td>
<td>2</td>
<td>(12)</td>
</tr>
<tr>
<td>(\text{S}_2\text{O}_8^{2-} + \text{HSO}_4^{-})</td>
<td>ACN</td>
<td>Tracer</td>
<td>Sulphate and sulphonate</td>
<td>Sulphate and sulphonate</td>
<td>1</td>
<td>Mostly sulphate in all conditions ((14),(15))</td>
</tr>
<tr>
<td>(\text{S}_2\text{O}_8^{2-} + \text{HSO}_4^{-})</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>Sulphate and sulphonate</td>
<td>Sulphate and sulphonate</td>
<td>2</td>
<td>((14),(15))</td>
</tr>
<tr>
<td>(\text{S}_2\text{O}_8^{2-} + \text{S}^{2-})</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Sulphate and sulphonate</td>
<td>Only sulphate</td>
<td>2</td>
<td>No sulphonate or hydroxyl end group ((15)). With Ag(^+) end group content reduces ((15))</td>
</tr>
<tr>
<td>(\text{S}_2\text{O}_8^{2-} + \text{metal ions})</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Sulphate and hydroxyl</td>
<td>Sulphate and hydroxyl</td>
<td>1</td>
<td>With Ag(^+) end group content reduces ((15))</td>
</tr>
<tr>
<td>(\text{S}_2\text{O}_8^{2-} + \text{amines})</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Sulphate and little OH</td>
<td>Sulphate and little OH</td>
<td>—</td>
<td>((15))</td>
</tr>
</tbody>
</table>

Hydroxyl end groups are practically non-existent in polymers obtained by using these redox initiator systems, persulphate-thio-sulphate being the only exception. The general absence of OH end groups in these polymers is probably due to the fact that the reducing sulphoxy compounds or radicals derived from them are very good scavengers of OH radicals.

Use of Na\(_2\)S as activator in redox persulphate initiation of MMA polymerization leads to incorporation of only hydrolysable sulphoxy end-groups in the polymer (Table 2). Sulphoxy end groups incorporated are, in this case, all sulphate and no sulphonate. Hydroxyl end groups are not found
RESULTS OF END GROUP ANALYSIS

in the polymers. It is not possible on the basis of dye tests to say anything about the incorporation of sulphide end groups in the polymers, since organic sulphides are not generally sensitive to the dye tests.

Polymerization by persulphate is catalysed markedly when Ag$^+$ or Fe$^{2+}$ ions are present and the polymers obtained are found to give responses for both sulphate and hydroxyl end groups. The comparatively low sulphate end group content (Table 2) in polymers initiated by the Ag$^{+}$–S$_2$O$_8^{2-}$ system is probably due to the fact that Ag$^+$ is a good scavenger of sulphate ion radicals (Ag$^+$ + $\cdot$SO$_4^{2-}$ → Ag$^{2+}$ or Ag$^{3+}$) and that the OH radical is generated by reaction of high-valent silver ions with water. This we have confirmed by independent experiments using trivalent silver complexes as initiator.

The fact that persulphates introduce OH end groups under acid conditions and SO$_4^{2-}$ end groups under alkaline conditions, is also demonstrated by the use of hydrazine hydrate (N$_2$H$_4$·H$_2$O) and hydrazine sulphate (N$_2$H$_4$·H$_2$SO$_4$). In the former case, end groups incorporated are mainly sulphate, response to OH end groups being either negative or very faint, but in the latter case (under acidic conditions), incorporation of sulphate end group is suppressed largely. Polymerization with hydroxylamine sulphate also conforms to the same pattern as with (N$_2$H$_4$, H$_2$SO$_4$).

Use of diethylamine and triethylamine as activators has yielded polymers giving good response for sulphate end groups (Table 2). Hydroxyl end groups are found to occur at relatively low concentration of amines to an extent of about 0.2–0.4 per chain. No basic (amino) end group has, however, been found in these polymers.

Initiation by halogens as oxidants

Halogens such as Br$_2$, Cl$_2$ can initiate vinyl polymerization$^{18}$ in aqueous media in presence of various reducing agents such as Fe$^{2+}$, Ti$^{3+}$, NH$_3$ and various amines in aqueous media. According to Evans et al.$^{19}$ the initiating species is supposed to be a halogen radical

\[
\text{Fe}^{2+} + \text{Br}_2 \rightarrow \text{Fe}^{3+} + \text{Br}^+ + \text{Br}^-
\]

The end group studies (Table 3) of the resulting polymers by dye techniques indicate the presence of both halogen and OH radicals, the extent

<table>
<thead>
<tr>
<th>Initiating system</th>
<th>Monomer</th>
<th>Technique used</th>
<th>End group surmised</th>
<th>End group detected</th>
<th>No. of end-groups per chain</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{2+}$ + Br$_2$</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Br Halogen (Br or Cl)</td>
<td>Br or Cl and OH</td>
<td>2</td>
<td>(19)</td>
</tr>
<tr>
<td>Fe$^{2+}$ + halogen (bromine, chlorine)</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Br and amine</td>
<td>Bromine, OH and amine</td>
<td></td>
<td>(18)</td>
</tr>
<tr>
<td>Br$_2$ + aliphatic amines</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Br</td>
<td>Br and amine</td>
<td>Br and amine</td>
<td>(18)</td>
</tr>
</tbody>
</table>

Table 3. Initiation by halogens as oxidants

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of which is dependent on the initiator concentration. The generation of 
OH radical may be due to the radical displacement reaction by bromine
(or chloride) atoms on water molecules.

Use of alkyl amine as activator with halogens gives rise to the formation
of polymer containing OH, amine and halogen end groups; but with am-
monia as activator, only halogen end group is incorporated. The matter is
still under investigation.

**Initiation by higher valent metal ions as oxidant**

Higher valent metal ions such as Fe$^{3+}$, Ce$^{4+}$, Cu$^{2+}$ have also been inves-
tigated as oxidants in the presence of various reducing agents such as reducing
sulphoxy compounds, hydrazine, alcohols etc. FeCl$_3$, in conjunction with
reducing agents such as reducing sulphoxy compounds (bisulphite for ex-
ample), yields polymers with non-hydrolysable sulphoxy end groups$^{20a}$
(Table 4). This shows that sulphonate radicals are potent initiators of poly-
merization. Traces of Fe$^{3+}$ ion are known to catalyse the decomposition
of hydrogen peroxide and the generation of hydroxyl radical intermediates
has been proposed by several investigators. This has been quantitatively
confirmed by dye techniques$^9$ (Table I).

<table>
<thead>
<tr>
<th>Initiating system</th>
<th>Monomer</th>
<th>Technique used</th>
<th>End group surmised</th>
<th>End group detected</th>
<th>No. of end-groups per chain</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$ + reducing sulphoxy compounds</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Sulphoxy</td>
<td>Sulphonate</td>
<td>2</td>
<td>(20a)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + N$_2$H$_4$</td>
<td>MMA</td>
<td>Chemical Dye technique</td>
<td>Amine</td>
<td>Nitrogen</td>
<td>—</td>
<td>(22)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + N$_2$H$_4$ + H$_2$O (vac. sealed)</td>
<td>MMA</td>
<td>Chemical Dye technique</td>
<td>Amine</td>
<td>Little OH, no amine</td>
<td>—</td>
<td>(23)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + N$_2$H$_4$ + O$_2$</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Amine</td>
<td>Hydroxyl, no amine</td>
<td>1</td>
<td>(23)</td>
</tr>
</tbody>
</table>

There have been rather conflicting reports$^{21, 22}$ mostly based on a very
limited number of experiments regarding the nature of end groups in vinyl
polymers obtained by Cu$^{2+}$ - N$_2$H$_4$, H$_2$O systems. Oxygen has a pronounced
effect and it is essential to have minute traces of oxygen. Kapur and Menon$^{22}$
proposed on the basis of their experiments that the OH radical is the initi-
ating species when the reaction is conducted in presence of oxygen while,
in the absence of oxygen, the N$_2$H$_3$ radical is the initiating species. Our
investigations on the end group analysis$^{23}$ of the polymers obtained with
this initiator system reveal that, although the response to OH radical is
predominant while in presence of oxygen, and is very faint in almost oxygen-
free condition, no basic end group is found to be present by applying dye
tests.
RESULTS OF END GROUP ANALYSIS

Initiation by organic acids as reductants

Organic acids (monobasic, dibasic, polybasic, hydroxylic) have been used both as photo-initiators\(^{24}\) and also in redox combination with permanganate\(^{25}, 26\) or persulphate\(^{15}\). Mainly carboxyl end groups are found to be present in all the polymers (Table 5). Presence of hydroxyl end groups is also exhibited by polymers initiated by hydroxyacids. This provides a direct

<table>
<thead>
<tr>
<th>Initiating system</th>
<th>Monomer</th>
<th>Technique used</th>
<th>End group surmised</th>
<th>End group detected</th>
<th>No. of end-groups per chain</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic or saturated dibasic acid (hy)</td>
<td>MMA</td>
<td>Dye technique</td>
<td>COOH</td>
<td>COOH very little OH</td>
<td>1-0-1.2</td>
<td>(24)</td>
</tr>
<tr>
<td>Hydroxy acids:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) lactic</td>
<td>MMA</td>
<td>Dye technique</td>
<td>COOH and OH</td>
<td>COOH and OH</td>
<td>1</td>
<td>(24)</td>
</tr>
<tr>
<td>(b) citric</td>
<td>MMA</td>
<td>Dye technique</td>
<td>COOH and OH</td>
<td>COOH and OH</td>
<td>2.5-3</td>
<td>(24)</td>
</tr>
<tr>
<td>(c) tartaric</td>
<td>MMA</td>
<td>Dye technique</td>
<td>COOH and OH</td>
<td>COOH and OH</td>
<td>2.0-2.6</td>
<td>(24)</td>
</tr>
<tr>
<td>MnO(_4)(^-) + oxalic acid</td>
<td>MMA</td>
<td>Dye technique</td>
<td>COOH</td>
<td>COOH</td>
<td>1.0-1.3</td>
<td>(26)</td>
</tr>
<tr>
<td>MnO(_4)(^-) + lactic</td>
<td>MMA</td>
<td>Dye technique</td>
<td>COOH and OH</td>
<td>COOH and OH</td>
<td>1</td>
<td>(26)</td>
</tr>
<tr>
<td>MnO(_4)(^-) + citric</td>
<td>MMA</td>
<td>Dye technique</td>
<td>COOH and OH</td>
<td>COOH and OH</td>
<td>3.5</td>
<td>(26)</td>
</tr>
<tr>
<td>MnO(_4)(^-) + tartaric</td>
<td>MMA</td>
<td>Dye technique</td>
<td>COOH and OH</td>
<td>COOH and OH</td>
<td>2.5</td>
<td>(26)</td>
</tr>
<tr>
<td>S(_2)O(_8)(^2-) + oxalic acid</td>
<td>MMA</td>
<td>Dye technique</td>
<td>COOH and sulphate</td>
<td>COOH and OH</td>
<td>1.7</td>
<td>(26)</td>
</tr>
<tr>
<td>MnO(_4)(^-) + E.D.T.A.</td>
<td>MMA</td>
<td>Dye technique</td>
<td>COOH and OH</td>
<td>COOH and OH</td>
<td>2</td>
<td>(25)</td>
</tr>
</tbody>
</table>

Table 5. Initiation by organic acid as reductant

evidence for the generation of carboxyl-bearing radicals for non-hydroxylic acids and both carboxyl and hydroxyl radicals for hydroxylic acids during the decomposition (either photolytic or in presence of an oxidant) of carboxylic acids.

Initiation by sulphonyl compounds as reductant

A number of redox systems\(^{20a}\) with reducing sulphonyl compound as the reductant and either of the following as the oxidant have also been investigated (Table 6);

(i) higher valent metal ions, \(v\text{\textit{iz. Cu}}^2+, \text{Fe}^{3+}\) and \(\text{Ag}^+\) ion;
(ii) potassium chlorate, potassium bromate;
(iii) hydrogen peroxide;
(iv) Oxygen.

(i) Generally speaking, these metal ions accelerate polymerization. All the polymers are found to contain non-hydrolysable sulphonyl end groups with little or no OH.

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<table>
<thead>
<tr>
<th>Initiating system</th>
<th>Monomer</th>
<th>Technique used</th>
<th>End group surmised</th>
<th>End group detected</th>
<th>No. of end-groups per chain</th>
<th>Remarks &amp; Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reducing sulphoxy compounds (HSO_3^−, S_2O_3^{2−}, SO_4^{2−}, S_2O_5^{2−}) + metal ions (Cu^{2+}, Ag^{+}, Fe^{3+}) Bisulphite + KClO_3</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Sulphonate</td>
<td>Sulphonate</td>
<td>2</td>
<td>(20a)</td>
</tr>
<tr>
<td>Reducing sulphoxy compounds + KClO_3 or KBrO_3</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Sulphonate</td>
<td>Sulphonate and chloride Sulphonate</td>
<td>2</td>
<td>Little OH at low sulphoxy concentration but no halogen (20) (H_2O_2/sulphoxy) is the determining factor for respective end group content (20) In case of S_2O_5^{2−}, mainly sulphonate is present (20a)</td>
</tr>
<tr>
<td>Reducing sulphoxy compounds + H_2O_2</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Sulphonate and OH</td>
<td>Sulphonate and OH</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Reducing sulphoxy + oxygen</td>
<td>MMA</td>
<td>Dye technique</td>
<td>Sulphonate and OH</td>
<td>Sulphonate and OH</td>
<td>1.5-2</td>
<td></td>
</tr>
</tbody>
</table>

(ii) Initiation by ClO_3^− − HSO_3^− has been studied by several investigators, but very little attempt has been made on the exact nature of end groups incorporated in the resulting polymers. Firsching and Rosen\(^\text{17}\) using tracer techniques estimated both sulphur and chloride in the resulting poly(vinyl chloride) initiated by KClO_3^− − NaHSO_3. Our results with MMA polymers show the presence of only sulphonate end groups and no halogen end group. The mechanism of radical generation is likely to be as follows:

\[ \text{H}_2\text{SO}_3 + \text{ClO}_3^− \rightarrow \text{ClO}_2^− + \cdot\text{OH} + \text{HSO}_3 \]

(iii) Polymers obtained using the redox systems H_2O_2−NaHSO_3, H_2O_2−Na_2S_2O_3, or H_2O_2−Na_2S_2O_4 have been found to contain both hydroxyl and non-hydrolysable sulphoxy end groups. The hydroxyl end group content increases with increase in H_2O_2/sulphoxy ratio with corresponding decrease in sulphoxy end group.
RESULTS OF END GROUP ANALYSIS

(iv) The polymers obtained with \((O_2 + NaHSO_3)\) and \((O_2 + Na_2S_2O_5)\) systems have been found to contain both hydroxyl and non-hydrolysable sulphony end groups to an average total to about two per polymer chain. But polymers obtained with \((O_2 + Na_2S_2O_4)\) system have been found to contain only non-hydrolysable sulphony end groups to the extent of about two per chain. Mechanism of radical generation is evidently different in the last case. Dainton (in a private communication) suggests the following mechanism for initiation by bisulphite.

\[
HSO_3^- + O_2 \rightarrow HO_2 + SO_3^- \\
2HO_2 \rightarrow H_2O_2 + O_2 \rightarrow 2\dot{O}H + O_2
\]

Initiation by higher valent metal ions only

There are ample reports in the literature on the use of metal ions (in higher oxidation states) as thermal initiators of aqueous vinyl polymerization\(^{27-31}\); the use of Co\(^{3+}\), Ag\(^{3+}\), Ce\(^{4+}\), Mn\(^{3+}\) as initiators of aqueous polymerization are a few important examples. Some ferric salts\(^{32, 33}\) have been widely employed as aqueous photo-initiators of polymerization. Little direct evidence has so far been adduced regarding the end groups in the resulting polymers with respect to the initiating radical. Our results are shown in Table 7. The general mechanism appears to be the oxidation of

Table 7. Initiation by higher valent metal ions only

<table>
<thead>
<tr>
<th>Initiating system</th>
<th>Monomer</th>
<th>Technique used</th>
<th>End group surmised</th>
<th>End group detected</th>
<th>No. of end groups per chain</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl(_3) + hv</td>
<td>MMA</td>
<td>Chemical</td>
<td>Chlorine</td>
<td>Chlorine</td>
<td>2</td>
<td>(32)</td>
</tr>
<tr>
<td>FeCl(_3) + hv</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>Chlorine</td>
<td>Chlorine (trace)</td>
<td>0.3–2</td>
<td>(36)</td>
</tr>
<tr>
<td>Ce(SO(_4))(_2) in dil H(_2)SO(_4)</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>OH</td>
<td>OH</td>
<td>2</td>
<td>(27)</td>
</tr>
<tr>
<td>KMnO(_4) dil H(_2)SO(_4)</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>OH</td>
<td>OH</td>
<td>2</td>
<td>(27)</td>
</tr>
<tr>
<td>Ag(^{3+}) complex</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>OH</td>
<td>OH</td>
<td>1–1.5</td>
<td>(27)</td>
</tr>
<tr>
<td>Co(^{3+}) complex (trioxalato)</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>OH &amp; COOH</td>
<td>OH &amp; COOH</td>
<td>2</td>
<td>(27, 31)</td>
</tr>
</tbody>
</table>

water to OH radicals, as evidenced by the presence of hydroxyl end groups in the resulting polymers\(^{27}\). Our results show that initiation by Ce\(^{4+}\) ions is through the agency of OH radicals\(^{27, 34}\) while initiation by an electron transfer between Ce\(^{4+}\) ion and monomer is suggested by Edgecombe and Norrish\(^{35}\), and Ananthnarayanan and Santappa\(^{35a}\).

Polymers obtained by photoinitiation with Fe\(^{3+}\) salts (both chloride and perchlorate) are found to contain both chlorine and hydroxyl end groups by applying dye techniques\(^{36}\). The chlorine content is usually rather
low and is dependent on the concentration of the initiator used. The presence of only chlorine atom end groups in these polymers as detected by Evans using chemical means seems to be not generally true.

**Initiation by reducing anions and cations alone**

Aqueous vinyl polymerization is also known to be readily induced by certain reducing anions such as bisulphite (HSO$_3^-$)$^{20e}$ and dithionite (S$_2$O$_4^{2-}$)$^{37}$. Polymers obtained by initiation with bisulphite or dithionite are found to contain non-hydrolysable sulphonate or similar end groups but no hydrolysable sulphate end groups (*Table 2*). This indicates that sulphonate

<table>
<thead>
<tr>
<th>Initiating system</th>
<th>Monomer</th>
<th>Technique used</th>
<th>End group surmised</th>
<th>End group detected</th>
<th>No. of end groups per chain</th>
<th>Remarks &amp; Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO$_3^-$aq.</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>Sulphonate</td>
<td>Sulphonate</td>
<td>2</td>
<td>(20b)</td>
</tr>
<tr>
<td>S$_2$O$_4^{2-}$</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>Sulphonate</td>
<td>Sulphonate</td>
<td>2</td>
<td>(37)</td>
</tr>
<tr>
<td>Cu$_2$Cl$_2$(aq.) alone</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>Cl and OH</td>
<td>Sulphonate</td>
<td>2</td>
<td>Initiation through hydrogen atom (38, 39) (40a)</td>
</tr>
<tr>
<td>Cu$_2$Cl$_2$ in acid (N$_2$ flushing)</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>Cl and OH</td>
<td>OH</td>
<td>2</td>
<td>(0-1 to 0-2) OH</td>
</tr>
<tr>
<td>Cu$_2$Cl$_2$ in acid (vac sealed)</td>
<td>MMA</td>
<td>Dye techniques</td>
<td>Cl and OH</td>
<td>OH</td>
<td>2</td>
<td>(40a)</td>
</tr>
</tbody>
</table>

radicals are responsible for initiation of polymerization. The simplest idea seems to be a redox reaction between reducing sulphoxy (say bisulphite) anion and the monomer leading to the formation of initiating bisulphite radicals. The overall reaction can be written as

$$2\text{HSO}_3^- + >C = C< + 2\text{H}_2\text{O} \rightarrow 2\text{HSO}_3^- + >\text{CH—CH}< + 2\text{OH}^-$$

Inoue *et al.*$^{38,39}$ reported that copper powder or cuprous chloride readily polymerize MMA in acid aqueous media and suggested that the initiation occurred through the agency of hydrogen atoms. This has not been substantiated by our results of end group analysis$^{40a}$. It has been found (*Table 8*) that only OH end groups are incorporated in cuprous initiated polymers obtained in acidic pH of the medium which has been profusely flushed with N$_2$ to exclude air or O$_2$. But polymers obtained in sealed tube experiments (which ensure more complete exclusion of oxygen), under otherwise identical conditions, contain very little OH end groups in them. Thus, generation of OH radicals and, hence, incorporation of OH and groups in these polymers depend largely on experimental conditions. Evidently the mechanism suggested by Inoue *et al.* appears to be primarily applicable in case where polymerization is conducted in rigorous absence of oxygen.
RESULTS OF END GROUPS ANALYSIS

Initiation by amino radicals

Davies et al.\textsuperscript{41} showed that the \(\text{NH}_2\) radical is the initiating species for the titanous–hydroxylamine system. But we could not detect enough basic end group in these polymers. In fact, it is rather difficult to introduce an amino end group into a polymeric chain by aqueous polymerization. However, we have recently been successful in introducing an amino end group in a polymer chain using the initiating system Fe\(^{3+}\) – thiourea\textsuperscript{40b}. This redox system gives a profusion of the \(\text{NH}_2\) bearing free radical which initiates polymerization. The matter is now under investigation.

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References