

# END-GROUP ANALYSIS OF POLYMERS BY INTERACTION WITH DYES

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## INTRODUCTION

A tell-tale birthmark is stamped on the extremity of almost every polymer chain and it is a challenge to the ingenuity of the chemists to detect and measure it. Fortunately, this birthmark is neither indelible nor immutable, and is amenable to normal chemical onslaught. Recent advances in functional group analysis are increasingly being pressed into service to do this delicate job and some degree of success has lately been achieved. Some recent illustrations using chemical and physical methods, include the determination of unsaturation by Entwistle<sup>1</sup>, sulphide end groups by Rosenthal, Frisone and Coberg<sup>2</sup>, alkoxy and fluorine groups by Bawn, Ledwith and Mathies<sup>3</sup>, and carboxyl in polytetrafluoroethylene by Bro and Sperati<sup>4</sup> as well as work by St. Pierre, Price and Sully<sup>5</sup>. Of course the tracer technique has long been employed for such purposes but its scope of application is rather limited and it is often incapable of giving results specific to the actual functional group.

Lately, we have developed two simple and rapid methods of detection of a few types of end groups based on dye-polymer interaction; these methods are called the "dye-partition test"<sup>6</sup> and "dye-interaction test"<sup>7</sup>, respectively. Since our method does not discriminate between an end group and a group present elsewhere in the chain, we shall use the general term (end) group to signify a functional group anywhere in the polymer chain. The details of the methods are given, or are to appear, elsewhere; in this paper, the principle is discussed briefly, followed by a discussion of some of the interesting results obtained so far with these methods. In quite a few cases the results are only fragmentary since the work is under active investigation.

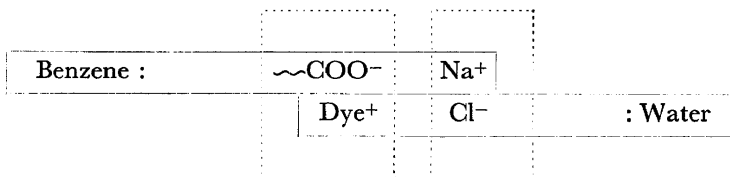
The importance of end group detection lies in the fact that it not only adds to our knowledge of the structure of the polymer molecule, but it often throws light on the mechanism of initiation, *vis-a-vis* the chemistry of free radicals. The speed with which our method can be carried out is an added advantage enabling a quick survey to be made over a wide field.

## DYE TESTS

### Dye-partition test

The dye-partition test depends on the following principle: if a benzene solution of a polymer which contains, say, an anionic end group is shaken

with an aqueous solution of a cationic dye, the dye goes into the benzene layer.



The coloration of the benzene 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 groups in polymers and can distinguish between strongly acidic and weakly acidic end groups. The same principle can also be applied to detergents, and has lately been extensively used in the analysis of ionic surface-active agents.

### Dye-interaction test

If an acid dye of fairly strong acidity is dissolved in an acid, a portion of the dye will be in the un-ionized acid form. If this solution is extracted with an immiscible solvent, *e.g.* benzene, the dye would pass into the benzene layer almost wholly in the un-ionized form. The un-ionized dye in the benzene layer, however, being of fairly high acid strength (but not of sufficient strength to exist by itself in the ionized form), has a strong tendency to pass into the ionic form, with a different colour, in the presence of a trace of base. This benzene extract of the dye would thus, be a reagent sensitive to colour change in presence of a minute trace of a base. In a sense, the dye may be regarded as an indicator of rather low  $pK$ , and the above expedient is essentially one for bringing the  $pK$  value to a much higher pH in an experimentally convenient range. Halogenated phthaleins, *e.g.* rose Bengal, erythrosin and eosins, have yielded satisfactory reagents of the above type.

Basic dyes behave similarly, and thus benzene extraction from alkaline solution of suitable basic dyes, under well-defined conditions, yields reagents which change colour in the presence of minute traces of acids. It follows from our principle that as quaternary basic dyes would be too basic to be suitable it is necessary to find dyes which are only moderately strong bases. Hence, secondary bases, methyl groups and anionic substituents would be expected to be structurally favourable: accordingly, Rhodamine 6Gx was found to yield a reagent which is sensitive to acids in almost micronormal concentration in benzene.

These reagents, in particular the Rhodamine reagent and the rose Bengal (or eosin) reagent, have been used extensively in our laboratory for end-group detection. The dye-interaction test (or "dye test" for short) is more elegant than the partition test, particularly as some polymers tend to precipitate at the interface in the partition test. However, the latter is more sensitive in the detection of a quaternary ammonium chloride end-group, and the two tests are often complementary to each other; when carried out on the same polymer they give much additional information.

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## AQUEOUS POLYMERIZATION

A large number of redox reactions (thermal or photochemical) are good polymerization initiators in aqueous media, and we have investigated many of them to ascertain the nature of the end group which they introduce into the resulting polymer. The most important and ubiquitous initiator in aqueous media is, of course, the hydroxyl radical, and polymers prepared in pure water by photo-initiation contain hydroxyl end-groups (*Table I*). However, the most readily available source of hydroxyl radicals is hydrogen peroxide.

*Table I.* Initiation by hydroxyl radical

(a) *Aqueous polymerization of methyl methacrylate in nitrogen atmosphere*

Initiators	Expected end group	Result of dye-interaction test*	$[\eta]$ in benzene at 35°C
(i) <i>Redox initiators at 30°</i>			
(1) $\text{FeSO}_4 + \text{H}_2\text{O}_2$	Hydroxyl	+++	0.7
(2) $\text{NaHSO}_3 + \text{H}_2\text{O}_2$	Hydroxyl Sulphite	+++ ++	— —
(3) $\text{N}_2\text{H}_4, \text{H}_2\text{O} + \text{H}_2\text{O}_2$	Hydroxyl Basic	+++ Negative	— 0.2
(4) $\text{FeCl}_3 + \text{H}_2\text{O}_2$	Hydroxyl	+++	0.5
(5) $\text{HCOOH} + \text{H}_2\text{O}_2$	Carboxyl	++	4.5
(ii) <i>Photo-initiators at 35–44°</i>			
(1) $\text{H}_2\text{O}_2 + \text{u.v. or sun}$	Hydroxyl	++	0.9–1.8
(2) u.v.	Hydroxyl	+	2.5
(3) $\text{Fe}(\text{ClO}_4)_3 + \text{sun}$	Hydroxyl	+++	1.85
(4) $\text{FeCl}_3 + \text{sun}$	Hydroxyl Chloride	+ +++	1.1
(iii) <i>Unstable metallic complex initiator at 30° in the dark</i>			
(1) $\text{Ag}^{3+}$ complex	Hydroxyl	++	4–4.5
(b) <i>Non-aqueous photopolymerization of methyl methacrylate in nitrogen atmosphere</i>			
(1) $\text{H}_2\text{O}_2$ (extracted by monomer and dried over anhyd. $\text{Na}_2\text{SO}_4$ ) + u.v. or sunlight or heat (60°C)	Hydroxyl	++	0.98 (sunlight polymer)

\* +, ++ and +++ indicate faint, strong and very strong positive test respectively

### Hydrogen peroxide systems

The classical Fenton's reagent ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ ) is known<sup>8,9</sup> to be a prolific source of hydroxyl radicals, and polymers produced with its aid contain many hydroxyl end-groups (*Table I*). A similar result is observed with other reducing agents, e.g.,  $\text{HSO}_3^-$ ,  $\text{NH}_2 \cdot \text{NH}_2$ . It is noteworthy that some sulphonate end groups are found with bisulphite and no basic end groups

with hydrazine. This may mean either that only hydroxyl radicals are produced, or that hydroxyl radicals are far more active than the other radicals present under the prevailing conditions.

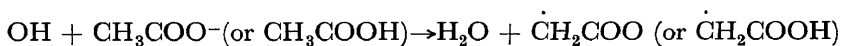
Hydrogen peroxide alone, irradiated by ultra-violet light is also a good source of hydroxyl radicals both in aqueous media and in non-aqueous media, and hydroxyl end groups are readily detected in the "aqueous" polymer, but only to a much smaller extent in the "non-aqueous" polymer. Surprisingly enough, thermal initiation by hydrogen peroxide is not possible in aqueous media, evidently due to inhibition by the liberated oxygen, but it takes place smoothly in non-aqueous media<sup>10</sup>, the end-group being hydroxyl at least in part. This may indicate that hydroxyl radicals have a longer life in non-aqueous media, or that hydrogen transfer occurs easily in a non-aqueous solvent.

The polymers obtained in all the above initiation reactions are of rather low molecular weight; the  $[\eta]$ -values are usually well below unity and only occasionally rise above unity. This gives the impression that hydroxyl radicals are also powerful chain-terminating agents. The fact that the tervalent silver biguanide complex in aqueous media produces polymers which bear hydroxyl end groups and are of exceedingly high molecular weight ( $[\eta]=4.45$ ) shows that this is not the sole factor involved. This may be due to a slow well-regulated supply of hydroxyl radicals in non-coagulating media. It is possible to derive another "aqueous" polymer of rather unusually high molecular weight from hydrogen peroxide-formic acid. The  $[\eta]$ -value is 4.5 and the end-group is predominantly carboxyl.

Table 2. Reaction of hydroxyl radicals

Initiators	Reaction	End group detected
(1) $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{Br}^-$	$\dot{\text{O}}\text{H} + \text{Br}^- \rightarrow \text{OH}^- + \dot{\text{B}}\text{r}$	$\text{Br} + +$
(2) $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{SO}_4^{2-}$	$\dot{\text{O}}\text{H} + \text{SO}_4^{2-} \rightarrow \text{OH}^- + \dot{\text{S}}\text{O}_4^-$	$(\dot{\text{S}}\text{O}_4)^- + + +$
(3) $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + (\text{COOH})_2$	$\dot{\text{O}}\text{H} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{OH}^- + \text{CO}_2 + \dot{\text{C}}\text{OO}^-$	$\text{COOH} + +$
(4) $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{CH}_3\text{COOH}$	$\dot{\text{O}}\text{H} + \text{CH}_3\text{COOH} \rightarrow \text{H}_2\text{O} + \dot{\text{C}}\text{H}_2\text{COOH}$	$\text{COOH} + +$

Some simple reactions of hydroxyl radicals can be easily demonstrated (Table 2). Thus, if bromide ion is present, much bromide end-group is detectable in the polymer. Evidently, the electron transfer reaction,  $\text{OH} + \text{Br}^- \rightarrow \text{OH}^- + \text{Br}$ , has taken place. Another easily demonstrable electron transfer reaction is that between hydroxyl and sulphate ( $\text{OH} + \text{SO}_4^{2-} \rightarrow \text{OH}^- + \text{SO}_4^-$ ), *i.e.* the Fenton reaction in the presence of sulphate anion; the polymer gives a strong positive test for strong acid end-groups. Similarly, the hydroxyl radical reacts with oxalic acid giving a polymer with carboxyl end groups and the reaction appears to be  $\text{OH} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{OH}^- + \text{CO}_2 + \text{CO}_2^-$ . A reaction which can be easily demonstrated is that between a hydroxyl radical and acetate ion (or acetic acid). The polymers contain carboxyl end groups and so the reaction is



**Oxalic acid systems**

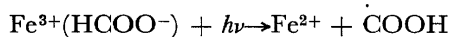
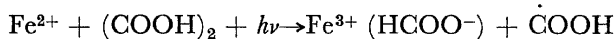
Just as hydrogen peroxide,  $\text{OH}\cdot\text{OH}$ , serves as a rich source of hydroxyl radicals, oxalic acid,  $\text{COOH}\cdot\text{COOH}$ , is a very convenient source of carboxyl radicals. The initiating reactions are similar and may be classified as thermal or photochemical reactions: (i) decomposition of oxalic acid  $(\text{COOH})_2 \rightarrow 2(\text{COOH}\cdot)$ , (ii) oxalic acid + a reducing agent, and (iii) oxalic acid + an oxidizing agent. These possibilities are easily realized experimentally and the polymer always gives a positive test for a carboxyl end-group (Table 3).

Table 3. Detection of end groups in poly(methyl methacrylate)

Catalyst or photosensitizer	Activator	End group tested for	End group detected	$[\eta]$ in benzene at 35°C
(1) $\text{KMnO}_4$	$\text{H}_2\text{C}_2\text{O}_4$	Carboxyl	Carboxyl	0.27
(2) —	$\text{H}_2\text{C}_2\text{O}_4$ + diffuse daylight	Carboxyl	Carboxyl	2.4
(3) Ferrous ammonium sulphate	$\text{H}_2\text{C}_2\text{O}_4$ + diffuse daylight	Carboxyl	Carboxyl	—
(4) $\text{K}_2\text{S}_2\text{O}_8$	$\text{H}_2\text{C}_2\text{O}_4$	Carboxyl sulphate	Carboxyl sulphate	1.9*
(5) —	$\text{Na}_2\text{C}_2\text{O}_4$ + diffuse daylight	Carboxyl sulphate	Carboxyl sulphate	—

\*Fractionated sample

Both oxalic acid and sodium oxalate can partake in photo-initiated polymerization forming polymers with carboxyl end-groups. The surprising feature of this photo-initiation is that  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , and other ions photosensitize the system to weak visible light. Thus, even an ordinary 100-watt bulb at a few cm distance from the Pyrex reaction vessel fully immersed in a water thermostat can easily bring about extensive photopolymerization in the presence of  $\text{Fe}^{2+}$  ions at concentrations as low as  $N/1000$ . As  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , and other ions are effective, it appears that photosensitization is involved, though a dissociative electron transfer mechanism as generalized by Dainton and James<sup>11</sup> can be formulated:



Oxidizing agents such as permanganate, manganese dioxide or persulphate can liberate carboxyl radical from oxalic acid. Such systems serve as initiators of polymerization, and, as expected, the polymer gives a positive test for carboxyl group.

**Persulphate systems**

Similar types of initiation in aqueous media should also be realizable from  $\text{S}_2\text{O}_8^{2-} = [\rightarrow 2(\text{SO}_4^-)]$  and  $\text{S}_2\text{O}_6^{2-} = [\rightarrow 2(\text{SO}_3^-)]$  ions. So far many reactions involving  $\text{S}_2\text{O}_8^{2-}$  have been investigated and the most unexpected

result is that polymers obtained after initiation by simple persulphate decomposition at about 25° or even lower temperatures show faint response for strong acid end groups (Table 4). The explanation would seem to be that the  $\text{SO}_4^-$  radicals rapidly react under the experimental conditions with either water or a monomer molecule forming other radicals which act as initiators of polymerization.

Table 4. Initiation by persulphate: aqueous polymerization of methyl methacrylate in nitrogen atmosphere

Initiator	Conditions of polymerization	Expected end group	Result of dye test*	$[\eta]$ in benzene at 35°C
(1) $\text{K}_2\text{S}_2\text{O}_8$ (0.1%)	30°C	Sulphate	Faint	2.9
(2) $\text{K}_2\text{S}_2\text{O}_8$ (0.1%)	50°C	Sulphate	++	1.25
(3) $\text{K}_2\text{S}_2\text{O}_8$ (0.1%)	Photochemical; Direct sunlight; Pyrex vessel	Sulphate	+++	0.95
(4) $\text{K}_2\text{S}_2\text{O}_8$ (0.1%) (in N/100 NaOH)	30°C	Sulphate	+	2.75
(5) $\text{K}_2\text{S}_2\text{O}_8$ (0.1%) (in N/100 $\text{H}_2\text{SO}_4$ )	30°C	Sulphate	Faint	3.25

\* ++, +++ indicate strong and very strong positive test respectively

However, if the same polymerization is conducted at 50°, the polymer gives a strong test for sulphate end-group. A strong response for sulphate end group is also obtained if the same reaction is carried out photochemically. A positive response is also given by the polymer obtained from catalytic decomposition by  $\text{Ag}^+$  ions.

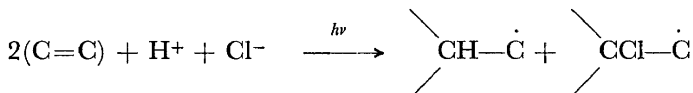
A large number of redox reactions of persulphate have been studied as initiators of polymerization in aqueous media. Here, again, some reactions give polymers with strongly acidic end-groups, whereas others give polymers with much less of such groups. Among the first group of reactions are: (i) persulphate-hyposulphite ( $\text{S}_2\text{O}_4^{2-}$ ), (ii) persulphate-thiosulphate, (iii) persulphate-metabisulphite, (iv) persulphate-bisulphite and (v) persulphate-diethylamine. Other redox pairs which behave similarly, though strong acid end groups are less pronounced in the resulting polymer, are persulphate-sulphur dioxide, persulphate-hydrogen sulphide (the polymer smells) and persulphate- $\text{Fe}^{2+}$ . In the second group of reactions which lead to polymers with faint response for strong acid end groups are included; (i) persulphate-alcohol, (ii) persulphate-formaldehyde, (iii) persulphate-formic acid or sodium formate, and (iv) persulphate-sodium oxalate. Probably persulphate may decompose by two mechanisms; in one of these the sulphate ion-radical has no free existence and the initiation is either by hydroxyl radicals or by transfer with the monomer.

### Photo-initiation by electrolytes

Ferric salts have been shown<sup>12, 13</sup> to be strong photo-initiators of polymerization in aqueous media; the mechanism is of the type,  $\text{FeCl}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \text{Cl}$ . We have investigated quite a few such cases for end groups and have obtained results in agreement with the above theory. Thus, polymers from ferric perchlorate give a strong test for hydroxyl end groups, whereas

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those from ferric chloride, and bromide give a strong test for halogen end groups. Surprisingly, photo-initiation was also observed with dilute hydrochloric acid, and chlorine end groups were detected in the polymer. The over-all reaction appears to be:



but the mechanism is uncertain; that suggested by Dainton and James<sup>11</sup> is possible. Some kind of anionic mechanism may also be involved. Another good photo-initiation is with dilute sulphuric acid, and little strong acid (end) groups are found in the polymer.

## NON-AQUEOUS SYSTEMS

### Chain transfer and copolymerization

The concept of chain transfer implies that the solvent is incorporated as end group. This assumption can be easily tested qualitatively by application of our method of end-group detection to many types of polymers. Halogenated solvents invariably show halogen end groups; hydroxylic and carboxylic solvents are often similarly incorporated. In the latter cases, preliminary results have shown some features which are not well understood. For example, polymers from *s*-butyl alcohol and isobutyl alcohol show a fairly strong positive test for hydroxyl groups, consistent with their high transfer constant, but the other alcohols show a rather poor response. It is possible that the intermediate alkoxy radicals derived from the latter alcohols lose a molecule of water before they attack a monomer. Carboxylic compounds also show similar anomalies; *e.g.* phenylacetic acid, which could not be made to enter a polymer chain by chain transfer to yield a carboxylic end group. It appears that the process of chain transfer is somewhat more complicated than has hitherto been envisaged.

Functional groups are also incorporated by copolymerization, and the presence of even minute quantities of units derived from added monomers can be demonstrated. Thus, the incorporation of allyl alcohol and allyl acetate even when present at concentrations as low as 1 mole per cent, can be easily demonstrated. The incorporation of common unsaturated solvents such as trichloroethylene, tetrachloroethylene, *etc.*, is also easily detected. Such results convincingly bring home the extraordinary reactivity of free radicals towards double bonds.

## UNSATURATION IN POLYMERS

We have recently been successful in developing two "dye test" methods for detecting unsaturation in high polymers. The first method involves the non-radical addition of hydrogen bromide to double bonds, and the detection of bromide by the dye-interaction test. The second method is based on the addition of butylamine to the double bond, a reaction developed by Entwistle<sup>1</sup>, and on the detection of the group thus introduced by means of the dye test. Some results of interest are presented in *Tables 5* and *6*.

Comparing thermal polystyrene with thermal poly(methyl methacrylate) by the above tests it is found that the former is practically free of double bonds while the latter is not. This is consistent with the previous observation<sup>14, 15</sup> that polystyrene terminates predominantly by coupling, whereas poly(methyl methacrylate) does so by disproportionation. On the other hand both the polymers obtained by emulsion polymerization are practically free from double bonds.

Table 5. Aqueous polymerization of methyl methacrylate in N<sub>2</sub> atmosphere (30°C)

Oxidant (0.1%)	Reductant	End group expected	Result of dye test*	[ $\eta$ ] in benzene at 35°C
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (0.02%)	Sulphate	+++	0.3
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (0.02%)	Sulphate	+	—
		Thiosulphate	+++	—
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH (0.1%)	Sulphate	+++	4.0
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	SO <sub>2</sub> gas	Sulphate	++	0.15
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Fe <sup>2+</sup> (0.0012%)	Sulphate	+	1.65
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	HCOOH (0.1%)	Sulphate	Positive	—
		Carboxyl	Negative	—
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	HCHO (0.1%)	Sulphate	+	2.8

\* +, ++, +++ indicate faint, strong and very strong positive test respectively

Table 6. Detection of double bonds

Polymers	Conditions of polymerization (°C)	Double bonds detected by HBr addition and sub- sequent testing by rhoda- mine reagent*	Double bonds detected by C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> addition and subsequent testing by eosin reagent*
(1) Poly(methyl methacrylate)	Thermal (60°)	++	++
(2) Poly(methyl methacrylate)	Emulsion polymerization at 30° using Cetavlon	Very faint	—
(3) Polystyrene	Thermal (60°)	Faintly positive	+
(4) Polystyrene	Emulsion polymerization at 30° using sodiumpalmitate	Very very faint	—
(5) Polystyrene	Same method at 30° using Cetavlon	Faintly positive	—

\* +, ++ indicate faint and strong positive test respectively

## QUANTITATIVE MEASUREMENT

Attempts have been made to develop the dye-interaction test quantitatively. This procedure has been successfully applied<sup>16</sup> for the estimation of ordinary acids and bases at nearly micronormal concentrations in benzene. The extension of this procedure to polymers has been attempted for carboxyl groups in an indirect way. Since it is difficult to obtain a polymer with a standard carboxyl content, we have determined  $r_1$  with the usual monomers as one component (M<sub>1</sub>) and some monomeric acids at about one mole per



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cent proportion as the other component ( $M_2$ ). Under such limiting conditions,  $r_1$  becomes equal to  $(M_2/M_1)_{\text{feed}}/(M_2/M_1)_{\text{polymer}}$ . Experiments have been carried out on eight such pairs, and the results are fairly satisfactory (Table 7); most of the  $r_1$  values agree fairly well with values reported in the literature<sup>17, 18</sup>. Considering the uncertainty in the arbitrary choice of the standard acid for comparison, and the scatter due to change in polymer concentration, the method can be regarded as giving a value which is only correct to within about twenty per cent in favourable cases. Naturally, many interesting applications can now be foreseen and work is in progress.

Table 7. Copolymer reactivity ratio  $r_1$  by the dye-interaction method

$M_1$	$M_2$	<i>Minimum</i> $M_2 : M_1$ in <i>copolymer</i> <i>(experimental)</i> $(10^{-2})$	$r_1$ <i>(experimental)</i>	$r_1$ <i>(literature)</i>
(1) Styrene	Acrylic acid	1.5	0.19	0.22, 0.15±0.01
(2) Styrene	Methacrylic acid	1.5	0.14±0.01	0.15±0.01
(3) Styrene	Crotonic acid	0.043	28	20
(4) Styrene	Itaconic acid	0.41	0.50	0.30
(5) Methyl methacrylate	Methacrylic acid	1.17	0.36±0.02	0.30±0.05
(6) Methyl methacrylate	Maleic anhydride	0.062	6.0	6.7±0.2
(7) Methyl methacrylate	Acrylic acid	0.203	1.28	—
(8) Vinyl acetate	Crotonic acid	0.81	0.32	0.33, 0.30±0.05

### Summary

The interaction between (end)groups of a polymer and a dye has been utilized for detection of polymer (end)groups by two different techniques called the "dye-partition test" and the "dye-interaction test" respectively.

The dye-partition test depends on the fact that if a solution (in chloroform or benzene) of a polymer containing an un-ionizable group is shaken at a suitable pH with an aqueous dye solution, the non-aqueous layer becomes coloured due to the dye forming a salt with the polymer. This test has been developed for carboxyl, sulphate and other strong acid groups, hydroxyl, amino, quaternary ammonium and halogen end-groups.

The dye-interaction test depends on the fact that benzene extracts of some dye solutions at a suitable pH have been found to give a colour change with extreme sensitivity in presence of acids, bases and salts in benzene solution though, normally, these dyes are insoluble in benzene and do not act as acid-base indicators in aqueous solution. These extracts have been utilized to test for the presence of the aforementioned groups in polymers.

The above (end)groups have been introduced in polymers by four general methods: (i) use of an initiator fragment containing the group; (ii) chain transfer with a solvent containing the groups, (iii) copolymerization with a trace of a monomer having the group; (iv) chemical transformation of an already existing (end)group in a polymer to another suitable for testing by the above methods.

*The results reported in this lecture are taken from papers presented in this symposium by P. Ghosh ( $r_1$  values), A. R. Mukherjee (hydroxyl end group), R. S. Konar (carboxyl end group) and M. K. Saha (halogen end group) in collaboration with the author, and from the unpublished results of S. C. Chadha (sulphate end group).*

### References

- <sup>1</sup> E. R. Entwistle. *Trans. Faraday Soc.*, **56**, 284 (1960)
- <sup>2</sup> I. Rosenthal, G. J. Frisone and J. K. Coberg. *Anal. Chem.*, **32**, 1713 (1960)
- <sup>3</sup> C. E. H. Bawn, A. Ledwith and P. Mathies. *J. Polymer Sci.*, **34**, 104 (1959)

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- <sup>4</sup> M. I. Bro and C. A. Sperati. *J. Polymer Sci.*, **38**, 289 (1959)
- <sup>5</sup> L. E. St. Pierre and C. C. Price. *J. Am. Chem. Soc.*, **78**, 3432 (1956)  
B. D. Sully. *J. Chem. Soc.*, **1950**, 1498; *Nature* **159**, 882 (1947)
- <sup>6</sup> S. R. Palit. *Makromol. Chem.*, **36**, 89 (1959); **38**, 96 (1960)
- <sup>7</sup> S. R. Palit. *Chem. & Ind. (London)*, **1960**, 1531; *Anal. Chem.* (1961) **33**, 1441 (1961)
- <sup>8</sup> F. Haber and J. Weiss. *Proc. Roy. Soc. (London)*, **A147**, 332 (1934)
- <sup>9</sup> J. H. Baxendale, M. G. Evans and G. S. Park. *Trans. Faraday Soc.*, **42**, 155 (1946)
- <sup>10</sup> U. S. Nandy and S. R. Palit. *J. Polymer Sci.*, **17**, 65 (1955)
- <sup>11</sup> F. S. Dainton and D. G. L. James. *Trans. Faraday Soc.*, **54**, 649 (1958)
- <sup>12</sup> M. G. Evans and N. Uri. *Nature*, **164**, 404 (1949)
- <sup>13</sup> M. G. Evans, M. Santappa and N. Uri. *J. Polymer Sci.*, **7**, 243 (1951)
- <sup>14</sup> J. C. Bevington, H. W. Melville and R. P. Taylor. *J. Polymer Sci.*, **12**, 449 (1954); **14**, 463 (1954)
- <sup>15</sup> C. H. Bamford and A. D. Jenkins. *Nature*, **176**, 78 (1955)
- <sup>16</sup> S. R. Palit and P. Ghosh. Paper presented at the *International Symposium on Microchemical Techniques*, University Park, Pennsylvania, August (1961)
- <sup>17</sup> T. Alfrey, Jr., J. J. Boherer and H. Mark. "Copolymerization", *High Polymers*, Vol. VIII, pp. 34-38, Interscience, New York (1952)
- <sup>18</sup> R. H. Boundy and R. F. Boyer. *Styrene, Its Polymers, Copolymers and Derivatives*, pp. 935-947, Reinhold, New York (1952)