

CHAPTER-VII

Endgroup Profile of Fractionated Polymers

Introduction

The endgroup profile of a polymer chain, formed during a free radical induced polymerization, is determined mainly by its termination mechanism and it is expected that endgroup content should not be less than one in any case, that one being the initiator fragment (or radical generated thereby) incorporated during initiation. If endgroup content is expressed in terms of initiation fragments only, the total endgroup content then will be one for unimolecular termination (by dissolved metal ions, etc.) and for bimolecular termination through disproportionations. But for bimolecular termination through combination and for primary radical termination, endgroup content will be two per chain. Endgroup content may be more than two, if there is branching in the chain. In case of chain transfer, however, solvent fragments would be incorporated in the chain, chain length would be drastically reduced and endgroup content may even be less than one.

In any polymerization process, the polymer chains produced consists of a multitude of molecular species covering a large range of sizes depending on the termination mechanisms simultaneously operative in each particular case. It is

normally presumed that the endgroup per chain is the same over the whole range of molecular weight in a particular run. The dye techniques have opened the possibility to test experimentally the above tacit assumption, and we have done so by fractionating the polymer covering comparatively narrow molecular weight ranges and vis-a-vis endgroup analysis of each fraction is estimated by the application of the dye techniques.

### Experimental

$\text{NaHSO}_3$ ,  $\text{CuSO}_4$ ,  $\text{FeCl}_3$ ,  $6\text{H}_2\text{O}$ , thiourea used as initiators were all of analytical grade. Polymers were prepared in aqueous or non-aqueous phase using the usual procedure as described in Chapter-II.

### Fractionation of Polymers

Polymer samples were fractionated by fractional precipitation method. For poly(methyl methacrylate) benzene and cyclohexane respectively, and for polystyrene benzene and methyl alcohol were taken as solvent and nonsolvent respectively. About one percent polymer solution was used and nonsolvent was added gradually until a slight turbidity develops. The solution was stirred slowly during precipitation. Then the precipitate was allowed to settle. After it has formed a coherent layer, which require about 2-3 hours, the supernatant

phase is removed by decantation. The amount of polymer in the polymer rich phase was determined by evaporation of solvent. More nonsolvent was added to the solution, the two phases separated by decantation, and the same process repeated.

### Endgroup Analysis

The different fractions of a fractionated polymer sample were subjected to endgroup analysis by using dye techniques as described in Chapter-II.

### Determination of Molecular Weight of Each Fraction

The molecular weight of each fraction of the polymer sample was determined by viscometric as well as osmometric studies to get an accurate molecular weight of the polymer sample.

### Results and Discussion

Results of different fractionated polymer samples are presented in Tables XIX, XX and XXI. The integral and differential distribution curves of different polymer samples are given in Figures VIII to XIII. With respect to endgroup per chain, a most unexpected results we have observed. The endgroup analysis shows that in all cases there is a















TABLE- XIX

Endgroup Picture of Fractionated Poly(methyl methacrylate)  
Initiated by NaHSO<sub>3</sub>

System : Aqueous Polymerization ;

MMA = 0.094 mole/litre ;

NaHSO<sub>3</sub> =  $2 \times 10^{-2}$  mole/litre

Isolation of Fractions : Solvent = Benzene ;

Nonsolvent = Cyclohexane ;

Temperature =  $30 \pm 0.1^\circ\text{C}$

Fraction No.	Cumilative weight %	$[\eta]$	$\bar{M}_n \times 10^5$	$\bar{M}_n \times 10^5$ (from osmometry)	O.D. of 0.1% solution at 660 m $\mu$	Sulfonate endgroup/chain
1	100	2.04	7.20	-	0.315	2.70
2	64.7	2.03	7.15	-	0.285	2.43
3	41.0	1.57	5.09	5.21	0.325	1.985
4	19.04	1.16	3.42	-	0.38	1.556
5	15.51	1.10	3.18	-	0.44	1.67
6	9.72	0.86	2.31	2.04	0.505	1.39
7	4.01	0.61	1.46	-	0.345	0.60

Average  $[\eta] = 1.52$ ,  $\bar{M}_n = 4.89 \times 10^5$

Sulfonate endgroup/chain = 1.60

TABLE-XX

Endgroup Picture of Fractionated Poly(methyl methacrylate)  
Initiated by  $\gamma\gamma'$ -Azo( $-\gamma$ -cyano-n-valeric acid)

System : Bulk Polymerization

$$(S)/(M) = 1.57 ;$$

$$\gamma\gamma' \text{-Azo}(-\gamma \text{-cyano-n-valeric acid}) = 3.57 \times 10^{-2} \text{ m/l}$$

$$\text{Temperature} = 50 \pm 0.1^\circ\text{C}$$

Isolation of Fraction : Solvent = Benzene ;

Nonsolvent = Cyclohexane ;

$$\text{Temperature} = 30 \pm 0.1^\circ\text{C}$$

Fraction No.	Cumulative weight %	$[\eta]$	$\bar{M}_n \times 10^5$	$\bar{M}_n \times 10^5$ (from osmometry)	O.D. of 0.2% solution at 515 $m\mu$	Carboxyl endgroup/chain
1	100	1.54	4.97	-	0.82	3.84
2	87	1.4	4.38	4.416	0.63	1.88
3	61.1	1.15	3.38	-	0.59	1.18
4	56.8	1.10	3.18	-	0.605	1.22
5	47.5	0.97	2.71	-	0.615	1.08
6	31.0	0.84	2.23	2.71	0.615	0.89
7	13.3	0.71	1.79	-	0.67	0.90
8	9.0	0.51	1.16	-	0.70	0.65

$$\text{Average } [\eta] = 0.094, \bar{M}_n = 2.59 \times 10^5$$

$$\text{Carboxyl endgroup/chain} = 1.2$$

TABLE-XXI

Endgroup Picture of Fractionated Poly(methyl methacrylate)  
Initiated by Fe<sup>3+</sup> - Thiourea Redox

System : Aqueous Polymerization ;

MMA = 0.094 mole/litre

Fe<sup>3+</sup> = 0.1 x 10<sup>-2</sup> mole/litre ;

Thiourea = 5.0 x 10<sup>-2</sup> mole/litre

Isolation of Fraction : Solvent = Benzene ;

Nonsolvent = Cyclohexane ;

Temperature = 30 ± 0.1°C

Fraction No.	Cumulative weight %	$[\eta]$	$\bar{M}_n$ x 10 <sup>5</sup>	O.D. of 0.05% solution at 630 m $\mu$	Amino endgroup/chain
1	100	1.7	5.66	0.20	2.55
2	71.99	1.3	3.97	0.16	1.39
3	49.1	1.08	3.11	0.18	1.24
4	36.4	0.83	2.2	0.19	0.94
5	31.07	0.74	1.89	0.185	0.80
6	24.7	0.54	1.25	0.273	0.75
7	5.04	0.29	0.549	0.64	0.66

Average  $[\eta]$  = 0.81,  $\bar{M}_n$  = 2.12 x 10<sup>5</sup>

Amino endgroup/chain = 1.7

monotonic decrease in the endgroup content per chain with the decrease in the molecular weight of each fraction. In all cases the endgroup contents per chain are the highest, even above two endgroups per chain for the highest molecular weight fraction and lowest e.g. below one, for the lowest molecular weight fraction.

From Table XIX where we have presented the data for seven fractions obtained from a poly(methyl methacrylate) sample prepared by aqueous initiation by  $\text{NaHSO}_3$  according to the method of Palit et al<sup>134</sup> we have noted that the sulfonate endgroup decreases monotonously from 2.7 to 0.6 with decrease in molecular weight. This is a very unexpected observation and we are heart put to find an explanation for the same. In aqueous polymerization according to Smith-Ewart theory endgroup should be two per chain, since the same radical initiates and terminates. Even if some unimolecular termination, not quite identified, was operative the endgroup per chain should not go below one for any sample and even then there is absolutely no reason for this biased behaviour with decrease in molecular weight.

This unusual result prompted us to find out whether this is a characteristic only of aqueous polymerization or this also happens in bulk polymerization. We studied a case of bulk polymerization using  $\gamma$ -azo(- $\gamma$ -cyano-n-valeric acid)

and results are presented in Table-XX. Here again the same features as in Table-XIX are observed and the highest molecular weight fraction has an unusually large namely 3.84 carboxylic endgroup per chain.

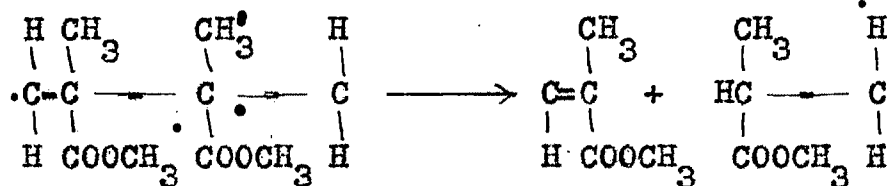
In case of  $\text{Fe}^{3+}$  - thiourea redox initiated polymerization, studied by us, the same trend of results are obtained as observed in previous cases. The results are presented in Table-XXI. As the results show the endgroup varies from 2.55 to 0.66 endgroup per chain.

As already mentioned it is difficult to find an explanation of the above facts based on the known mechanism of polymerization. The followings are the tentative suggestions and the relative importance of this could be ascertained only after more extensive works in this fields. The results by themselves are intriguing and appear to promise some vital changes in the details of the accepted mechanism of the polymerization.

Firstly, the bigger molecules in a polymer are produced mainly by combination leading to two endgroups per chain and the smaller molecules mainly by disproportionation resulting in incorporation of about one endgroup per chain.

Secondly, lower molecular weight fractions may be formed due to the breakdown of the abnormal link in the bigger polymer molecules which may result in the lowering of the

molecular weight as well as the endgroup content in the polymer sample. A probable equation of such dismutation is as follows:-



Thirdly, this phenomenon may be attributed to chain transfer. For the smaller molecules high monomer transfer is taking place leading to the lowering in the endgroup content per chain.

Fourthly, very high endgroup per chain e.g. above two, may be explained in terms of branching resulting in the dangling chains which may be due to chain transfer on the backbone of the polymer chain.