

CHAPTER-VI

Termination Reaction in Vinyl Polymerization

Introduction

The nature of termination reaction in vinyl polymerization is a matter of controversy. A number of methods have been used for distinguishing between the various possibilities¹²⁸⁻¹³². The problem of termination mechanism in vinyl polymerization can be approached by qualitative determination of the endgroup per chain in the polymer molecule. If termination takes place by exclusive disproportionation and exclusive combination then endgroup per polymer chain should be one and two respectively.

$\gamma\gamma'$ -Azo($-\gamma$ -cyano-n-valeric acid), soluble in non-aqueous solvents, undergoes thermal fission in the N-N bond, thereby generating two identical initiating carboxyl bearing radicals which can be estimated by applying our dye-techniques. In order to give an idea about the termination mechanism, $\gamma\gamma'$ -azo($-\gamma$ -cyano-n-valeric acid) in solution in dimethyl formamide and ethylene carbonate is selected as initiator and the termination mechanism has been suggested from the endgroup picture.

Experimental

Freshly distilled methyl methacrylate and styrene were used for polymerization experiment. Dimethyl formamide, Ethylene carbonate used as solvents were of analytical grade. $\gamma\gamma$ -Azo-(γ -cyano-n-valeric acid) was supplied by G.S. Misra from Lucknow University. Polymerization experiments were carried out in non-aqueous solution following the usual procedure described in Chapter-II.

Results and Discussion

The results of endgroup analysis of poly(methyl methacrylate) and polystyrene initiated by $\gamma\gamma$ -azo-(γ -cyano-n-valeric acid) in solution in dimethyl formamide and ethylene carbonate are presented in Tables XVI, XVII and XVIII. The results show that the carboxyl endgroup content in poly(methyl methacrylate) obtained in ethylene carbonate medium is nearly one per chain and that in polymers obtained in presence of dimethyl formamide as solvent is somewhat less in more or less comparable conditions otherwise. The lower carboxyl endgroup content in polymers obtained in dimethyl formamide media is presumably due to chain transfer effect by the solvent which hinders the normal incorporation of primary initiating radical and instead, some solvent fragments may have incorporated into the polymer chain. The effect of rather pronounced chain transfer by dimethyl formamide solvent

TABLE- XVI

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

System : Non-aqueous Polymerization ;
Solvent = Ethylene Carbonate ;
Temperature = $50 \pm 0.1^\circ\text{C}$

(S)/(M)	Initiator mole/litre $\times 10^2$	$[\eta]$	O.D. of 0.2% polymer solu- tion with rhodamine reagent	Carboxyl endgroup/chain
1.57	1.785	1.4	0.543	1.18
1.57	2.68	1.025	0.56	0.87
1.57	3.57	0.88	0.694	1.2
0.53	2.68	1.35	0.538	1.05
4.71	2.68	1.12	0.574	1.09

TABLE- XVII

Endgroup Analysis of Poly(methyl methacrylate) initiated
by $\gamma\gamma$ -Azo($-\gamma$ -cyano-n-valeric acid)

System : Non-aqueous Polymerization ;

Solvent = Dimethyl Formamide ;

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

(S)/(M)	Initiator mole/litre $\times 10^2$	$[\eta]$	O.D. of 0.2% polymer solu- tion with rhodamine reagent.	Carboxyl endgroup/chain
1.30	1.785	1.22	0.466	0.42
1.30	2.68	0.81	0.574	0.81
1.30	3.57	0.7	0.672	0.9

TABLE- XVIII

Endgroup Analysis of Polystyrene Initiated by
 $\gamma\gamma'$ -Azo($-\gamma$ -cyano-n-valeric acid)

System : Nonaqueous Polymerization ;
 Solvent = Ethylene Carbonate ;
 Temperature = $80 \pm 0.1^\circ\text{C}$

(S)/(M)	Initiator mole/litre $\times 10^2$	$[\eta]$	O.D. of 0.2% polymer solu- tion with rhodamine reagent	Carboxyl endgroup/chain
0.85	0.445	0.23	0.958	1.01
0.85	0.67	0.228	1.01	1.07
0.85	0.89	0.20	1.142	1.09
0.23	0.89	0.30	0.83	1.12
2.55	0.89	0.22	1.112	1.22

is clearly evidenced by the relatively low $[\eta]$ values for the polymers. This proves that in dimethyl formamide solvent, the carboxyl endgroup content is less due to chain transfer effect than that in polymers obtained in ethylene carbonate medium where the transfer is much less pronounced and is evidenced by relatively high $[\eta]$ values.

The presence of one endgroup per polymer chain in poly(methyl methacrylate) confirms that the termination in methyl methacrylate polymerization takes place through disproportionation as reported by earlier workers¹³¹⁻¹³³.

In case of polymerization of styrene, however, conflicting results are obtained. For this case also one endgroup per chain of polymer molecule is present indicating the termination through disproportionation. This is in contrast with the earlier findings¹³².