Diradical-Initiated Polymerization Mechanism

Bahattin BAYSAL

The Institute of Physical Chemistry, Science Faculty, University of Ankara

Özet : — Radikallerle başlatılan polimerizasyon reaksiyonlarında iki çeşit başlama (initiation) kademesi ileri sürülmektedir. Monoradikallerin başlattığı polimerizasyon reaksiyonları dikkatle incelenmiş ve muhtelif kademelere ait hız sabitleri çeşitli metodlarla tayin edilmiştir.

Diradikallerle başlatılan polimerizasyon kinetiği ise henüz aydınlatılmış değildir. Termal ve fotokimyasal polimerizasyonu izah için, eksite edilen karbon-karbon çifte bağında diradikal teşekkülüne ait ileri sürülen hipotez denel olarak gerçeklenememiştir.

Bir monomer molekülünde çifte bağın açılması ile, monomerin iki tarafına doğru büyüme imkânına sahip bir diradikal meydana gelebileceği gibi, polimerik yapıda fakat kararlı olmayan bir molekülün parçalanması ile de diradikal meydana gelebilir. Birinci tipde diradikallerin büyüme ve sonlanma imkânları statistik bakımdan daha önce incelenmiştir. Bu çalışmada problem kinetik olarak ele alınmış, yalnız zincir transferinin (chain transfer) polimer moleküllerinden sorumlu olduğu düşüncesinden hareket edilerek, hesaplanan diradikal konsentrasyonunun yüksekliği ve başlama reaksiyonuna ait aktivasyon enerjisinin küçüklüğü sebebiyle bunun mümkün olamıyacağı gösterilmiştir.

Polimerik yapıda bir katalizörün polimerizasyona etkisi, monomerde çözünen, metil metakrilat peroksidin katalizör olarak kullanılması ile bu çalışmada ilk defa incelenmiştir. Neticeler diradikal çoğalma (propagation) reaksiyonunun ceryanını teyid etmemiştir. Zincir transferi polimerizasyon derecesini kontrol etmektedir.

INTRODUCTION

Two kinds of initiation reactions considered in polymerization. Usual catalysts give monoradicals which can start polymerization by adding monomer molecules to only one side of radical fragments. The role played by such radicals having a single free valency in polymerizing systems has now been established and rate constants for different steps are calculated using various methods. To explain uncatalyzed thermal and photochemical polymerization a mechanism involving diradical formation as the initial step has been postulated. The electronic structure of the carbon-carbon double bond has been elucidated by quantum mechanical treatment by the methods of atomic and molecular orbitals. The energy levels of the unsaturation electrons are given for the normal and excited states of ethylen molecule by Eyring *et al.* (¹). The existence of a low-lying triplet state in excited double bond favors diradical formation. The role played by these diradicals in polymerization is still not entirely clear. It is necessary to distinguish between two types ot diradical. Firstly, there are those which may be formed by the stepwise decomposition of a polyfunctional or polymeric catalyst. In this case two free valencies will not normally coexist. Secondly there are true biradicals which would be formed by the opening of a double bond. In each case free valencies can add monomer units and form a polymer molecule growing at both ends.

The possibility of diradical initiation was discussed recently. The problem has technical importance as well as theoretical. Using diradical producing initiator one may perhaps obtain rapid polymerization without sacrificing chain length.

Polymeric phthalic peroxide was used as a diradical initiator for the polymerization of styrene by Tobolsky and his co-workers (³). However, this catalyst is not initially soluble in monomer and the obtained results attributed to ordinary gel effect by Vaughan (⁴).

Behaviour of the second type diradicals was widely discussed by Haward (⁵). He compared the self-termination reaction in a growing diradical polymer chain with bimolecular termination between different polymer molecules. The ratio

$$\frac{\text{Rate of self-termination of diradical chains}}{\text{Rate of termination by different chains}}$$

was calculated succesfully from the statistical considerations and the results were applied to the thermal polymerization of styrene. The numerical value of the above ratio under certain conditions is about two thousand. This indicates that if diradical initiation can ever start, diradical chains would terminate by self combination.

In another new paper Zimm and Bragg (6) find a competition between self-termination and chain propagation reactions. Using rate constants for propagation and termination reaction of polymerization they showed that self-termination is much more rapid than chain propagation, for any degree of polymerization less than 520 for styrene diradicals. Steric hinderance should prevent self-termination of very small diradical chains. If some of these diradical chains can transfer activity to a monomer molecule the resultant monoradicals can initiate a polymerization of the ordinary kind, leading to a product of high molecular weight.

Using rate constants $k_p = 367$ and $k_t = 1.87 \times 10^7$ for polymerization of methyl methacrylate (7) at 60°C and M = 8.95 (all units are moles/liter and seconds) we calculated $\mathrm{I} = 133$, the corresponding polymerization degree value for methyl methacrylate below which self-termination rate is grater than chain propagation. (We assumed that freely moving link length *b* for methyl methacrylate is not much different than the value obtained for styrene, because densities and molecular weights are very near to each other for these two monomers).

Zimm and Bragg calculated that for the thermal polymerization of styrene at 60°C the low molecular weight fraction would be 29% of the whole polymer. However, careful investigations which have been carried out for fractionation and molecular weight distribution of poly methyl methacrylate do not indicate the presence of such a low molecular weight material. (8,9).

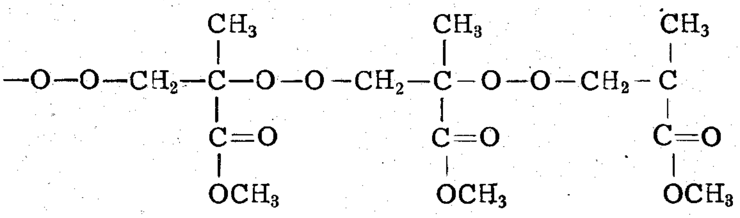
We will give additional information about the non-possibility of such a low molecular fraction in the following pages of this paper.

The thermal rate in styrene and methyl methacrylate polymerization is so slow that it does not give any basic data for kinetic comparison with catalyst polymerizations. But photo initiated polymerization elucidates some interesting points. Tobolsky and his co-workers (10, 11) have indicated that diradical growing would be distinguishable from monoradical initiation in its effect on the relation between the reciprocal of the degree of polymerization, $1/P_n$ and the rate of polymerization, R_p; polymerization initiated by ultraviolet light defines the same relation as the monoradical catalyst. The runs giving high polymerization rates were not fully succesfull it looked very interesting to use a poly peroxy catalyst as a polymerization initiator.

Experimental

The methyl methacrylate peroxide was prepared by heating purified methyl methacrylate at 40°C in a dark oven for ten days (12). Peroxidic monomer was concentrated at 40°C bath temperature under reduced pressure to a gummy residue. Final solvent traces were removed at room temparature and 1 mm. pressure overnight.

Considering the polymeric nature of methyl methacrylate peroxide, the following structure would be the most likely interpretation of our material:



$$-O-O-CH_2-\underset{\substack{|\\ C=O\\ |\\ OCH_3}}{\overset{\substack{CH_3\\ |}}{C}}-O-O-CH_2-\underset{\substack{|\\ C=O\\ |\\ OCH_3}}{\overset{\substack{CH_3\\ |}}{C}}-O-O-CH_2-\underset{\substack{|\\ C=O\\ |\\ OCH_3}}{\overset{\substack{CH_3\\ |}}{C}}$$

The methyl methacrylate used in the polymerization was Rohm and Haas Co. material and contained 0.006% hydroquinone. It was distilled in a pyrex apparatus at a boiling point of 46.0 - 46.5°C at 100 mm. Hg.

About 10 g. methyl methacrylate containing an appropriate poly peroxy catalyst was put in pyrex glass tubes. The tubes were placed in Dry Ice and sealed *in vacuo*. They were then placed in an oven at 60°C and polymerization was allowed to proceed for the requisite time period. At the end of reaction monomer-polymer mixture was cooled and polymer was precipitated from methanol. The precipitated polymer was filtered, and then dried overnight in vacuum at 60°C.

Using chloroform as a solvent intrinsic viscosities were determined in Ostwald viscometers at 20°C.

Degree of polymerization, P_n is calculated from intrinsic viscosity using following relation which was given for unfractionated poly methyl methacrylate (13):

$$[\eta] = 2.52 \times 10^{-3} P_n^{0.80}$$

Experimental results are given in Table I.

Table I.

Polymerization of Methyl Methacrylate at 60.0°
by Poly Methyl Methacrylate Peroxide

Expt. No.	Catalyst initial concn. (gr./100cc)	Yield (Wt. %)	Time (min.)	$R_p \times 10^5$ (mol $\times$ l^{-1}.sec^{-1})	$[\eta]$	$(1/\bar{P}_n)10^4$
1	0.08	3.64	425	1.31	10.0	0.30
2	0.20	3.95	267	2.22	6.75	0.50
3	0.40	7.72	425	2.73	5.30	0.68
4	1.00	6.59	194	5.10	3.40	1.18
5	1.00	2.97	74	6.01	3.20	1.36
6	1.20	10.4	240	4.74	3.20	1.36
7	2.00	10.2	240	6.51	2.05	2.23

Table II. shows thermal polymerization of methyl methacrylate at 60°C under various experimental conditions. Runs No. 1 and 2 were carried out in vacuum, i.e. dissolved oxygen was removed from the medium. Run No. 3 contains only dissolved air in monomer, there is not a gas phase above the liquid.

Table II.

Thermal Polymerization of Methyl Methacrylate at 60°
Under Various Conditions

Expt. No.	Condition	Yield (Wt. %)	Time (min.)	$R_p \times 10^5$ (mol $\times$ l^{-1}. sec^{-1})	$[\eta]$	$(1/\bar{P}_n)10^4$
1	Twice Degassed	0.38	180	0.265	10.1	0.29
2	» »	0.37	180	0.260	10.1	0.29
3	Under Dissolved air	21.8	1320	2.48	10.1	0.29
4	Under Dissolved oxygen	1.30	720	0.272	6.7	0.50
5	» »	1.44	646	0.336	8.2	0.39

Run No. 4 and 5 contain dissolved oxygen in monomer, there is not a gas phase in these runs either.

For these thermal runs intrinsic viscosity determinations and molecular weight calculations were carried out in the same way as given above.

Discussion

In Fig. 1 we draw the monoradical and the two limiting diradical lines which were obtained and described in a previous paper, for methyl methacrylate polymerization(⁹). Experimental points corresponding to the poly peroxy catalyst are given by circles with horizantal lines.

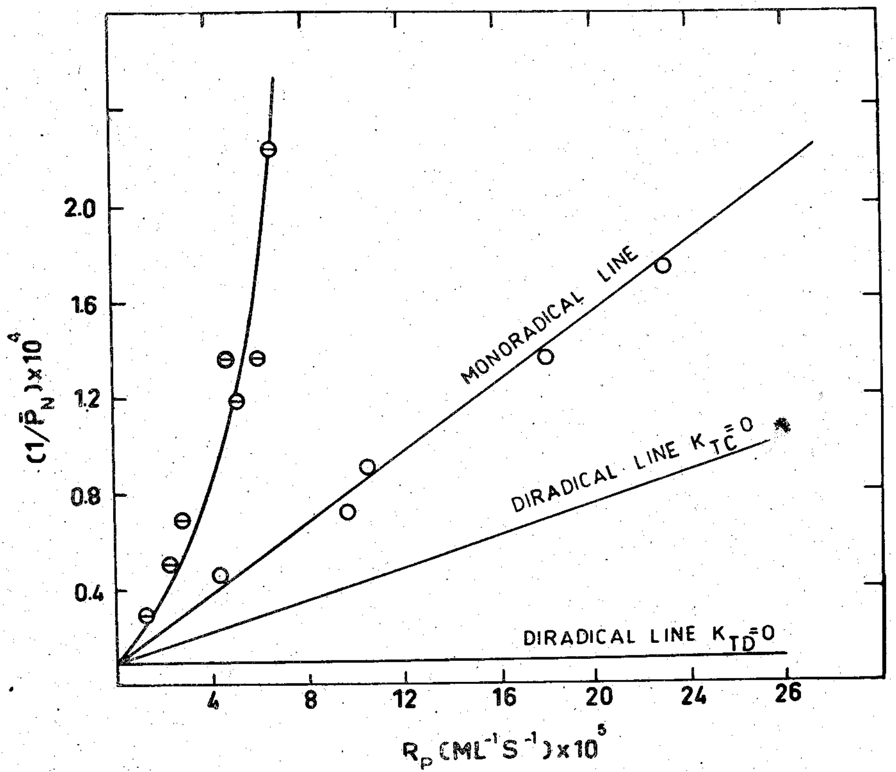


Fig. 1. Reciprocal degree of polymerization, $1/P_n$, *versus* rate of polymerization, R_p, for polymerization of Me-Methacrylate.
Θ — Experimental points, catalyst by poly methyl methacrylate peroxide.

From the structure of poly peroxy catalyst one can expect diradicals which will initiate polymerization by adding monomers on both ends.

If diradical growing did actually occur, the graph defined by $1/P_n$ versus R_p as obtained from the experimental results would be somewhere between the two limiting lines shown in Figure 1.

It seems from the Figure 1. that poly peroxy catalyst shows a clear chain transfer to initiator. Howewer, in this effect the share of the impurity of catalyst could not be distinguished.

Thermal polymerization of methyl methacrylate which contains different amount of oxygen was investigated. We expect to obtain higher rates but constant polymerization degree by increasing the oxygen concentration, due to the diradical tendency of the oxygen molecule. Though the rate of polymerization increases by increasing the oxygen concentration as it will be seen from Table II, P_n decreases, so that chain transfer controls the molecular weight in this case also.

In the earlier pages of this paper we discussed the possibility of diradical initiation and competition between the self-termination and bimolecular termination (5). We also took into consideration the calculation that indicates, as pointed out by Zimm and Bragg (6), that the self termination of a diradical is much more rapid compared with chain propagation reaction. According to Ziegler(14) ring formation falls sharply after the 6 membered ring and reaches a minimum for the 9-10-11 membered rings. If we combine this fact with experimental results of fractionation of thermal polymers which show no indication for the low molecular material, we can come to the conclusion that only dimers and trimers were formed if diradicals ever formed and started growing. High molecules are generated only if one of these active valencies is transferred to monomer.

In the thermal polymerization, supposing that high molecules can only generated if one of active valencies is transferred to a monomer molecule from a diradical, we can try to calculate diradical concentration under these assumptions.

Using initial rates of polymerization, R_p, values we made an attemp to calculate diradical concentration in the thermally polymerizing system:

$$R_p = k_p [C^*][M] \qquad (1)$$

where k_p is propagation rate constant, $[C^*]=$ monoradical concentration, $R_p = 0.21 \times 10^{-5}$ mol/literxsec. for thermal polymerization of styrene at 60°C (15). From the above relation $[C^*] = 1.43 \times 10^{-9}$ mol/liter. Diradical concentration $[C^{**}]$ would be equal to $[C^*]/C_m = 0.24 \times 10^{-4}$ mol/liter, where C_m is the chain transfer constant to monomer (15). Supposing a diradical will arise from a dimolecular collision of monomer molecules it may be possible to write the following relation

$$R^{**} = k_i [M]^2 \qquad (2)$$

where R^{**} is rate of initiation of diradicals and k_i, the rate constant for these reactions.

It is possible to assume $C^{**} = R^{**}$ under steady states conditions. This relation gives us the possibility of calculation k_i values in reaction (2), from over all rate of polymerization R_p.

Numerical calculations are given in Table III for 60°C.

Table III.

	$R_p \times 10^5$ (mol/1×sec)	C^*	C_m (mol/l.)	k_i
Styrene	0.21	1.43×10^{-9}	6×10^{-5}	3.29×10^{-7}
Me-Methacrylate	0.26	0.81×10^{-9}	1×10^{-5}	10.1×10^{-7}

The thermal polymerization of styrene and methyl methacrylate was ivestigated in a large temperature scale. A review article will appear soon (16). Activation energies for propagation steps of these monomers were also given in literature.

Therefore we were able to calculate the activation energies for diradical initiation, based on the assumption that diradicals terminate when they are di- or tri- mers and only chain transfer to monomer initiates polymerization.

Calculated values are the following :

Styrene $k_i = 4.0 \times 10^{-3} e^{-899/RT}$
Me-Methacrylate $k_i = 7.9 \times 10^{-4} e^{-917/RT}$

(Reproducibility of thermal rates are extremely sensitive to reaction procedure for Methyl methacrylate ; in this case we only considered the data given by Walling and Briggs (17).)

The experimental fact that a small amount of an inhibitor prohibits the polymerization reactions is an obvious contradiction to these very low activation energies. This results implies that either diradicals do not initiate at all, or if they ever can initiate and start growing one end would lose its activity immediately.

REFERENCES

(1) H. M. Hulbert, R. A. Harman. A. V. Tobolsky and H. Eyring Ann. N. Y. Acad. Sci. **44**, 371 (1943).

(2) D. H. Hey, A. V. Tobolsky Discussion of Faraday Soc. 2 2338 (1947).

(3) H. A. Shah, F. Leonard and A. V. Tobolsky J. Polymer Sci. VII, 537 (1951).

(4) M. F. Vaughan J. Polymer Sci. VIII, 445 (1952).

(5) R. N. Haward Trans. Faraday Soc. XLVI, 204 (1950).

(6) B. H. Zimm. J.K. Bragg. J. Polymer Sci. IX, 476 (1952).

(7) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart J. Am. Chem. Soc. **74**, 497 (1949).

(8) F. M. Billemeyer Jr. and W. H. Stockmayer J. Polymer Sci. V. 121 (1950).

(9) I. Harris, R. G. J. Miller, J. Polymer Sci. VII. 391 (1951).

(10) D. H. Johnson and A. V. Tobolsky J. Am. Chem. Soc. **74**, 938 (1952)

(11) B. Baysal and A. V. Tobolsky

(12) C. E. Barnes, R. F. Elofson and G. D. Jones J. Am. Chem. Soc. **72**, 210 (1950).

(13) B. Baysal and A. V. Tobolsky J. Polymer Sci. IX, 171 (1952).

(14) K. Ziegler, Ber. 67, A 139 (1934).

(15) F. R. Mayo, R. A. Gregg and M. S. Matheson J. Am. Chem. Soc. **73** 1691 (1951).

(16) B. Baysal and A. V. Tobolsky J. Polymer Sci. in press.

(17) C. Walling and E. Briggs J. Am. Chem. Soc. **68**, 1141 (1946).

(Manuscript received 1 April 1952)