

## **Termination mechanism of polymethyl methacrylate and polystyrene studied by ultrasonic degradation technique**

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### **Summary**

A new method for determining the dominant termination mechanism in radical polymerization based on ultrasonic scission of long chains is used to study the termination of polystyrene and polymethyl methacrylate. The method is extended to obtain the disproportionation/combination ratio. Long dead polymer chains in solution were broken by ultrasound. The chain radicals thus formed were then allowed to terminate in the presence and absence of a chain terminating agent (radical trap). The resulting molecular weights are compared to find the dominant termination mechanism. It is found that the dominant mechanism in polystyrene is combination and that in polymethyl methacrylate is disproportionation. These results are in accordance with those quoted in the literature and obtained by other methods. The effectiveness of the radical trap used (2-chloroethyl benzene) was tested by NMR and it was found that when the trapping agent is present it terminates 100% of the polymethyl methacrylate chains. The time evolution of the degree of polymerization was compared to simulations based on Schmid's model. The disproportionation/combination ratios were found for polymethyl methacrylate as 2 and for polystyrene as 1/7 respectively through simulation studies.

### **Introduction**

Polymer sonochemistry has been an active field since Demann and Asbach used ultrasound (US) for polymerization in 1930's<sup>1-3)</sup>. Keiqiang, Malhorta, Berlin, Kruus, Hatate and others can be cited among the researchers who have worked in this field<sup>4-20)</sup>. It is generally accepted that the cause of ultrasonic depolymerization is cavitation or shock waves generated during US application<sup>1-3)</sup>.

When a long chain polymer is sonicated it is known that it preferentially breaks at the middle and long chain radicals result<sup>4,5)</sup>. During the depolymerization of PMMA, PS and PVA Tabata at all have shown the formation of macroradicals using ESR techniques<sup>6,7)</sup>. Investigating the sonication in the presence of the radical scavenger diphenyl picryl hydrazil (DPPH) resulted in two DPPH molecules per bond<sup>1,2)</sup>.

The two different types of termination processes, namely disproportionation and combination result in different groups at the end of the polymer chain. Presence of such groups effects the polymer properties. The unsaturated end group in the

disproportionation case has an initiating effect in thermal degradation, branching, gelation and polymerization. The termination step is especially important to control the degree of polymerization  $P_n$  in the absence of dominant transfer reactions. The nature of the termination reaction is extremely important for both theoretical considerations and practical applications.

There are several techniques available for measuring disproportionation / combination (d/c) ratios. Calculating from the degree of polymerization, kinetic method, coupling experiments, grafting tests, gelation tests and using bifunctional initiators or labeled initiators are some of them<sup>21-27)</sup>.

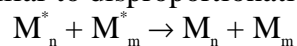
In a previous work we proposed a method for determining the dominant termination mechanism based on breaking the chains by US and used it for ethyl methacrylate<sup>28)</sup>. In this technique, first high molecular weight polymer is obtained, precipitated, filtered and dried. Then the polymer is solved in toluene and sonicated. Polymer chains are broken by US and the radicals thus formed are allowed to terminate in the presence and absence of a radical trap, in this case 2-chloro ethylbenzene(CEB). While breaking the long polymer chains by US,



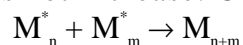
the addition of CEB terminates rapidly the reactions of the radicals generated by ultrasonic chain scission via the following mechanism.



This reaction mechanism is similar to disproportionation



in that molecular weight does not increase. On the other hand combination mechanism



increases the molecular weight by joining the chains. Since there are no monomers in the sonication medium only these scission and termination reactions take place. Radical growth is not allowed. If the dominant termination mechanism is disproportionation then the newly formed radicals terminate without combining whether radical trap is present or not. The final  $P_n$  is independent of the presence of the radical trap. If, on the other hand, the dominant termination mechanism is combination, the presence of the radical traps will suppress the combination step and the resulting molecular weight will depend on the presence of the radical traps. The main advantage of this method over the traditional ones is that the tests are performed after the polymerization is completed, the polymers precipitated and redissolved. Thus the reaction environment is free of monomers, initiators and oligomers. Chain transfer reactions to monomer and initiator are absent. The only reactions are chain scission by US, disproportionation, combination and termination with a radical trap.

The evolution of the  $P_n$  depends on the scission mechanism<sup>29-36)</sup>. Schmid has proposed a model based on experimental data. In Schmid's phenomenological model for concentrated solutions the number of scissions per unit time varies as

$$\frac{dS}{dt} = k \ln(P_{nt}/P_{n0}) \quad (1)$$

Here S is the number of scissions per unit time per unit volume, k is a constant,  $P_{nt}$  and  $P_{n0}$  are the values of  $P_n$  at time t and at the start of the reaction respectively.

In this work this technique is used to determine the dominant mechanism in PS and PMMA. In addition to the experimental work simulations based on Schmid's model for concentrated solutions were performed phenomenologically to estimate the d/c ratio.

## Experimental

### Materials:

2,2'Azobisisobutyronitrile (AIBN) from K&K laboratories was recrystallized twice from methanol (m.p. 101.5 C). Methyl methacrylate (MMA) and styrene (S) (from Aldrich) were freed from inhibitor by treating with 10% aqueous sodium hydroxide solution and washed with distilled water several times until the water used came out neutral. After drying with anhydrous calcium sulfate overnight the monomer was fractionally distilled in vacuo.

### Depolymerization:

Very high molecular weight polymethyl methacrylate (PMMA) (MW=2300000) and polystyrene (PS) (MW=1600000) were prepared and depolymerization studies followed in an US bath (80W, 35kHz) at 20°C. Two identical groups of polymer solutions (12g/l polymer in toluene) were prepared and saturated with N<sub>2</sub> bubbling for 15 mins. CEB was added into one group of samples as a radical trap. Samples with and without CEB are exposed to US for 30, 60, 90, 120 and 150 mins. The solution viscosity and molecular weight of each sample were determined at the end of each period. The solution viscosity was determined by Ubbelohde type viscometer and the mean value of five measurements was used in molecular weight determination. Molecular weight equations are given below

$$[\eta] = 9.39 \times 10^{-3} \bar{M}_v^{0.68} \quad \text{for polymethyl methacrylate}$$

$$[\eta] = 19.5 \times 10^{-3} \bar{M}_v^{0.635} \quad \text{for polystyrene}$$

The NMR measurement was made in acetone solution with a Bruker HG1513 instrument.

## Simulations

The time evolution of the P<sub>n</sub> was compared with simulations. Schmid's model for concentrated solutions was taken as basis in the simulation studies. The kinetic equations corresponding to chain scission, combination, disproportionation and termination by a radical trap are integrated by Runge Kutta method to follow the evolution of the numbers of the three species in the reaction medium.

The reactions considered during degradation studies and their effect on depolymerization medium are given below. The notation used is as follows, [P], [R], [D] and [C] are the concentrations of dead polymers, radical chains, diradical chains and the total number of chains respectively and n<sub>p</sub>, n<sub>r</sub> and n<sub>d</sub> are the corresponding numbers used in simulations. k<sub>td</sub>, k<sub>tc</sub> and k<sub>tr</sub> are the termination rate constants for disproportionation, combination and trapping respectively.

### Chain scission reactions

1. dead chain scission: one dead chain → two radical chains



$$n_r \rightarrow n_r + 2, \quad n_p \rightarrow n_p - 1, \quad R_{ps} = S[P]/[C] \quad (2b)$$

2. radical chain scission: one radical chain → one radical chain + one diradical chain



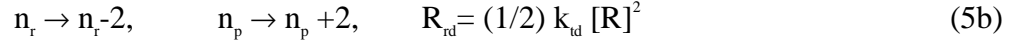


3. diradical chain scission: one diradical chain  $\rightarrow$  two diradical chains



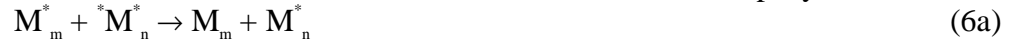
*Disproportionation reactions:*

4. two radical chain disproportionation: two radical chains  $\rightarrow$  two dead polymer chains

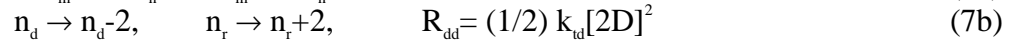


5. one radical chain, one diradical chain disproportionation:

one radical chain + one diradical chain  $\rightarrow$  one radical chain + one dead polymer

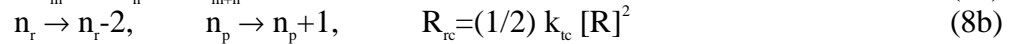


6. two diradical chain disproportionation: two diradical chains  $\rightarrow$  two radical chains



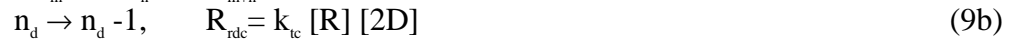
*Combination reactions:*

7. two radical chain combination: two radical chains  $\rightarrow$  one dead polymer chain

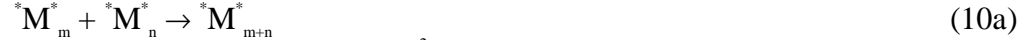


8. one radical one diradical chain combination:

one radical chain + one diradical chain  $\rightarrow$  one radical chain



9. two diradical chain combination: two diradical chains  $\rightarrow$  one diradical chain



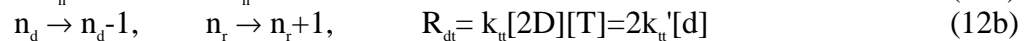
*Termination with terminating agent:*

10. radical chain termination: one radical chain  $\rightarrow$  one dead polymer chain



Here [T] is the terminating agent concentration. Since it is very high it can be assumed to be constant.

11. diradical chain termination: one diradical chain  $\rightarrow$  one radical chain



Here the scission probabilities of an average dead chain, an average radical and an average diradical are assumed to be the same.

In the presence of a radical trap(CEB) the time dependence of the chain concentration is given by,

$$\frac{d[C]}{dt} = S \quad (13a)$$

$$\frac{d[S]}{dt} = k \ln (P_{nt} / P_{n0}) \quad (13b)$$

Here it is assumed that the concentration of the traps is sufficiently high and every chain is trapped before it has time to recombine. The two parameters governing this reaction are;  $S_0$ , the initial value of the chain scission rate and  $k$  the Schmid parameter.

The time dependence of the concentrations of the three species of chains in the absence of radical traps that result from the above reactions is given by,

$$\frac{d[P]}{dt} = -S \frac{[P]}{[C]} + \left(\frac{k_{tc}}{2} + k_{td}\right)[R]^2 + 2k_{td}[R][D] \quad (14a)$$

$$\frac{d[R]}{dt} = 2S \frac{[P]}{[C]} - (k_{tc} + k_{td})[R]^2 + 4k_{td}[D]^2 \quad (14b)$$

$$\frac{d[D]}{dt} = S \left(1 - \frac{[P]}{[C]}\right) - 2(k_{tc} + k_{td})[R][D] - 2(k_{tc} + 2k_{td})[D]^2 \quad (14c)$$

$$\frac{d[S]}{dt} = k \ln(P_{nt}/P_{n0}) \quad (14d)$$

These reactions are governed by four parameters. These are  $k_e$  and  $k_d$  the rate constants for combination and disproportionation in addition to the two parameters  $S_0$  and  $k$ .

The Eqs. 13. and 14. were integrated numerically by the Runge-Kutta method to simulate the time evolution of the  $P_n$  for the cases with and without radical traps respectively. If only chain scission reaction is allowed so that the radicals formed can not combine then the behavior of the  $P_n$  will be identical to the experimental case where the addition of radical traps immediately terminates any radical before any combination takes place. In simulations the initial scission rate parameter  $S_0$  and the Schmid parameter  $k$  giving its time dependence were chosen to be appropriate for the experiment with radical traps. These parameters were then used unchanged for the cases with the combination and disproportionation reactions.

In Schmid's model the number of chain scissions per unit time decreases as long as  $P_n$  remains below the initial value. For this reason this model is not realistic on long time-scales. Simulation runs were terminated when the number of chain breakages per unit time reached zero.

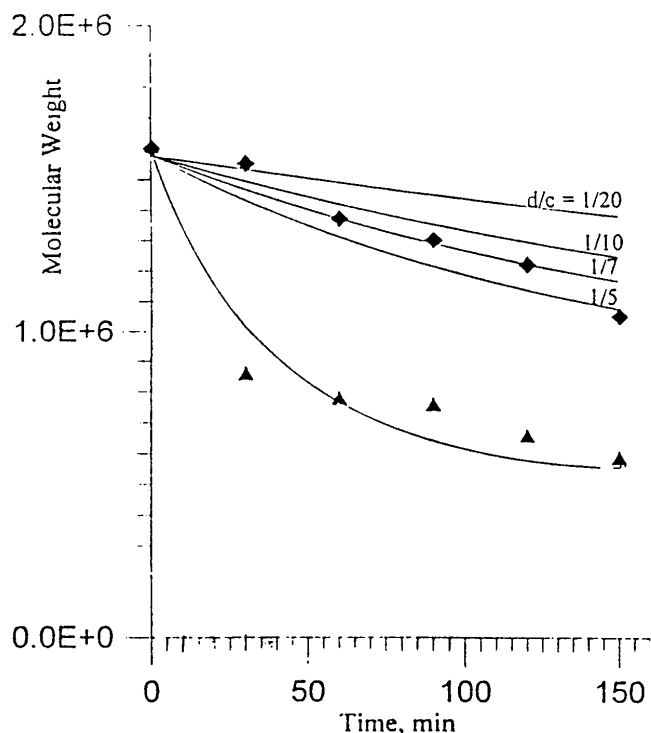
## Results and discussion

There are no monomers, initiators and catalysts in the sonication medium as a result there are no growing radicals and scission and termination are the only reactions allowed. The stress due to US application is most intense at the middle of the chain and the scission takes place preferentially at the middle<sup>1-5</sup>. For this reason the results of this method do not depend on whether the chain ends are saturated or unsaturated. In methods which determine the termination mechanism by thermal degradation of polymers special care must be given to these effects<sup>37</sup>.

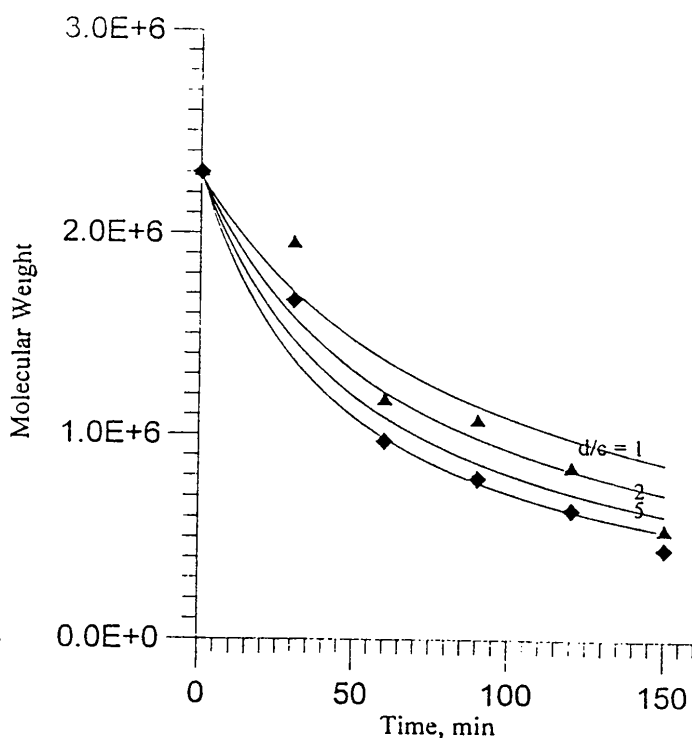
In Fig. 1. the number average molecular weights of depolymerized PS samples in the presence and absence of CEB are given. Molecular weights of CEB terminated samples are nearly half of the freely terminated samples, combination is the dominant termination

mechanism. Theoretical curves for  $d/c$  ratios of 1/5, 1/7, 1/10 and 1/20 are given in the Fig. 1. The curve for  $d/c$  for 1/7 best represents the data. The Fig. 1. indicates that the  $d/c$  ratio of PS is between 1/10 and 1/5.

In Fig.2. the number average molecular weights of depolymerized PMMA samples in the presence and absence of CEB are given. The samples terminated with CEB and terminated freely follow almost the same path. Disproportionation is the dominant termination mechanism.



**Fig. 1.** Number average molecular weights of depolymerized PS samples in the presence and absence of CEB, denoted by triangles and squares respectively. Lines represent simulated data corresponding to  $d/c$  ratios of 1/5, 1/7, 1/10 and 1/20.



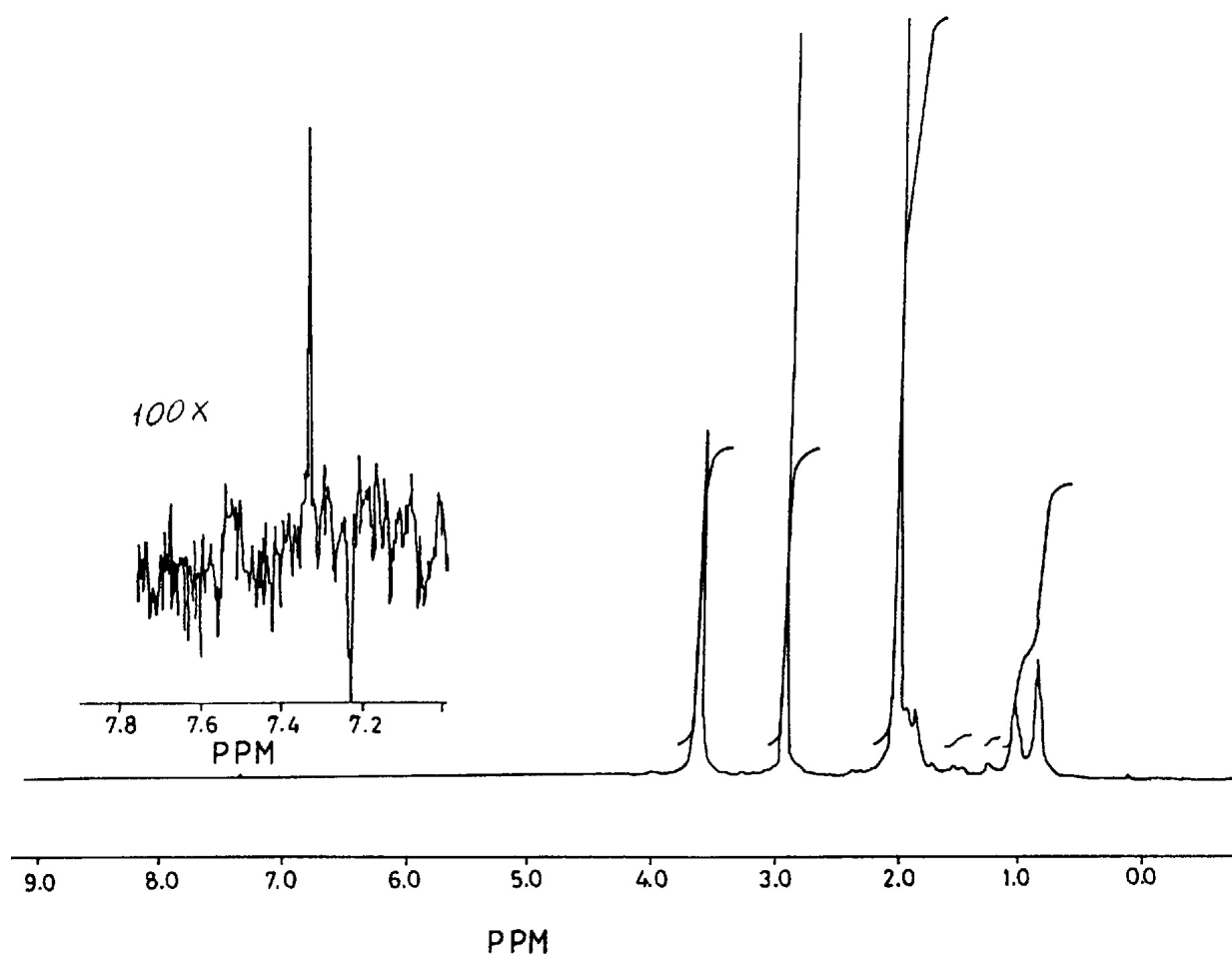
**Fig. 2.** Number average molecular weights of depolymerized PMMA samples in the presence and absence of CEB, denoted by squares and triangles respectively. Lines represent simulated data corresponding to  $d/c$  ratios of 1, 2 and 5.

As the time evolution of the PMMA samples was only slightly influenced by the addition of CEB we checked its efficiency as a radical trap. One of the CEB terminated (150 mins.) PMMA samples was analyzed with NMR. The results are given in Tab. 1. and Fig.3. The molecular weight of this sample has been found as 450000 by viscometry. Since the original molecular weight was 2300000 it is seen that the number of molecules has increased by a factor of five. The NMR results obtained from peak integrals gives molecular weight of 560000, indicating that 80% of the chain ends have a radical trap attached. Since 1/5 of the ends are the ends of the original chains we can conclude that within experimental error all radicals have been terminated by CEB.

The very rapid drop in the molecular weight observed in the PMMA experiment and the similarity of the evolution of the molecular weight with and without CEB (Fig.2.) seemed to indicate a clear domination of disproportionation over combination. However simulations show that this data is best represented by a d/c ratio of 2. The values between 3/2 and 3 are also acceptable. These results show that breaking the polymer chain by US is a simple, straightforward and reliable method for determining the termination mechanism in radical polymerization and comparison of experimental results with simulations is seen to be very useful in interpreting the results.

**Table 1.** NMR data for CEB capped PMMA sample exposed to US for 150 mins.

<u>PPM</u>	<u>Integral</u>
7.3384	0.006
3.6174	10.220
2.9165	8.622
1.0364	3.304
0.8539	5.705



**Fig.3.** NMR spectrum of the CEB capped PMMA sample exposed to US for 150 mins.

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