ARI The Bulletin of the Istanbul Technical University VOLUME 54, NUMBER 2
Communicated by A. Nihat Berker

Obtaining the Ratio of Termination Rate Constants of Poly (Methyl Methacrylate) by the Ultrasonic Scission Method

Ayşegül Öncül-Koç
Faculty of Sciences and Letters, Bahçeşehir Üniversitesi, Bahçeşehir 34590, Istanbul, Turkey
Ahmet Giz and Huceste Çatalgil-Giz
Department of Physics, Istanbul Technical University, Maslak 34469, Istanbul, Turkey
(Received 20 December 2003)

The termination step in radical polymerization occurs either by combination or by disproportionation. The termination mechanism of poly (methyl methacrylate) in sonochemical environment is studied by the ultrasonic scission method. The method is improved to give quantitative results by incorporating non-linear least squares analysis of the data. The Chi square map obtained by fitting the data to Schmid's equation gives the ratio of the rate constants for termination by disproportionation and by combination as $k_{td}/k_{tc} = 2.6 \pm 0.4$.

Keywords: Termination, disproportionation, combination, chain scission, ultrasound

1. Introduction

Sonication of a polymer solution decreases the molecular weight of the polymers by breaking the backbones of long chains. The exact mechanism of polymer scission during sonication is still debated. It is clear that cavitation is the main cause of chain scission. The debate is on the relative importance of various cavitation effects. The scission is generally attributed to the implosion of cavitation bubbles which cause such effects as the extreme temperatures and pressures, the shock waves that emanate from the implosions or the turbulence caused by the interaction of the shock waves [1]. However it was recently demonstrated that under conditions which do not allow implosions, resonant oscillation of the bubbles can also lead to chain breakage [2-4].

It is also known that the stress due to ultrasound (US) application is most intense at the middle of the chain, the backbones of long polymer chains are broken preferentially around the middle [5, 6] and chains shorter than a minimum length are immune to US effects. Molecular weight of the sonicated sample approaches a limiting molecular weight in a stretched exponential form.

Several theoretical and phenomenological models have been developed to describe the molecular weight evolution during sonication. Doulah's model [7, 8] attributes the scission to the viscous forces created by the turbulence due to shock waves formed by implosions. Since the model incorporates a mechanism it also makes predictions on the evolution of the molecular weight distribution (MWD) as well as the mean molecular weight. Glynn's model [9, 10] gives a better MWD evolution but lacks a limiting molecular weight.

The phenomenological model used here, proposed by Schmid [11, 12], gives neither the MWD nor a mechanism but gives a good description of the decrease of mean molecular weight [1]. Since our data involves M_v, the viscosimetric average molecular weight, this model was preferred. Schmid's model has the added advantage that it is simple and incorporating the effects of termination reactions is straightforward.

In radical polymerization, growing chains terminate either by combination or by disproportionation. The two different types of termination processes, result in different groups at the end of the polymer chain. In initiator derived polymerizations, combination results in a single polymer molecule with two initiator fragments, one at each end of the chain. Disproportionation creates two polymer molecules, only one end of each has an initiator group. One of these chains has an unsaturated unit and the other has a saturated unit on the other end. So the mode of termination plays an important role in determining the polymer end groups. Presence of such groups effects polymer properties. The unsaturated end group has an initiating effect in thermal degradation [13-16], branching [17-19], gelation and polymer-

$$\begin{array}{lcl} & CH_3 & CH_3 \\ & | & | \\ R-CH_2- & C-CH_2- & C-R' \\ & | & | \\ & C=O & C=0 \\ & | & | \\ & O-CH_3 & O-CH_3 \end{array} \xrightarrow{US} \begin{array}{lcl} & CH_3 & & CH_3 \\ & | & & | \\ R-CH_2- & C* \quad + & *CH_2- & C-R' \\ & | & & | \\ & C=O & & C=O \\ & | & & | \\ & O-CH_3 & & O-CH_3 \end{array} \quad (1)$$

ization. It is reported that head-to-head linkages which occur in combination create weak points in methyl methacrylate chains. In poly(methyl methacrylate) head to head bonds are reported to be thermally unstable at elevated temperatures and prone to unzipping [13-16]. The termination step is especially important in controlling the degree of polymerization, (P_n) and the molecular weight distribution 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 (k_{td}/k_{tc}) 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 [20-26]. However since the kinetics of sonochemistry are different from ordinary chemistry it is not clear that the termination rate constants and ratios obtained by other means are applicable in sonochemistry. For this reason it is important to have a sonochemical method to determine the constants if they are to be used in sonochemical studies.

US and radical traps have recently been used in combination for forming block copolymers [27-29] US application in the presence and absence of a radical scavenger and deducing the k_{td}/k_{tc} therefrom, have been reported previously, for poly (ethyl methacrylate), polystyrene and poly (methyl methacrylate). In this technique, first high molecular weight polymer is obtained, precipitated, and dried. Then the polymer is dissolved in an apolar solution and sonicated. Polymer chains are broken by US (Eq. 1).

The radicals thus formed terminate either by disproportionation reactions such as,

$$\xrightarrow{k_{td}} \quad R-CH= \begin{array}{l} CH_3 \\ | \\ C \quad + H_3C- \\ | \\ C=O \\ | \\ O-CH_3 \end{array} \begin{array}{l} CH_3 \\ | \\ C-R' \\ | \\ C=O \\ | \\ O-CH_3 \end{array} \quad (2a)$$

$$\xrightarrow{k_{td}} \quad R-CH_2- \begin{array}{l} CH_2 \\ || \\ C \quad + H_3C- \\ | \\ C=O \\ | \\ O-CH_3 \end{array} \begin{array}{l} CH_3 \\ | \\ C-R' \\ | \\ C=O \\ | \\ O-CH_3 \end{array} \quad (2b)$$

whereby the molecular weight does not increase or by combination reactions like,

$$\xrightarrow{k_{tc}} \quad R-CH_2- \begin{array}{l} CH_3 \\ | \\ C-CH_2- \\ | \\ C=O \\ | \\ O-CH_3 \end{array} \begin{array}{l} CH_3 \\ | \\ C-R' \\ | \\ C=O \\ | \\ O-CH_3 \end{array} \quad (2c)$$

which increase the molecular weight by joining the chains. Addition of a chain capping agent, in this case(2-chloroethyl)benzene (radical trap, T)rapidly terminates the reactions of the radicals generated by ultrasonic chain scission (Eq. 3)
The effect of this reaction mechanism is similar to disproportionation in that the molecular weight does not increase. In the sonication medium, only these scission and termination reactions take place. Radical growth is not possible. If the only termination mechanism is disproportionation, then the newly formed radicals terminate without combination whether a radical trap is present or not. The final molecular weight is independent of the presence of the radical trap. If,

$$R-CH_2- \begin{array}{c} CH_3 \\ | \\ C-CH_2- \\ | \\ C=O \\ | \\ O-CH_3 \end{array} \begin{array}{c} CH_3 \\ | \\ C-R' \\ | \\ C=O \\ | \\ O-CH_3 \end{array} \xrightarrow{US,T} R-CH_2- \begin{array}{c} CH_3 \\ | \\ C-T \\ | \\ C=O \\ | \\ O-CH_3 \end{array} + T-CH_2- \begin{array}{c} CH_3 \\ | \\ C-R' \\ | \\ C=O \\ | \\ O-CH_3 \end{array} \quad (3)$$

on the other hand, the termination mechanism is combination, the presence of the radical traps will cause the molecular weight evolution to differ from the case with no traps. Thus comparison of the molecular weight evolution in the presence and absence of radical traps enables determination of the k_{td}/k_{tc}. The main advantage of this method over the traditional ones is that the experiments are performed after the polymerization is completed, the polymers precipitated and redissolved. 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 degree of polymerization depends on the scission and termination mechanism.

In this work this method is improved to give quantitative results. Experimental scission data are obtained by periodically sampling the sonication medium (with the radical traps) and performing viscosimetric measurements. The error bars are found by repeating each molecular weight measurement 5 times.

The χ^2 appropriate for a set of Schmid parameters S_0 and k, were determined by comparing the experimental molecular weight data with numerical solution of Schmid's equation with that set of parameters. A χ^2 map was then plotted by sweeping over the parameter space.

A similar procedure, using the best fit values of the auxiliary variables thus obtained, was then used to compare the data with no traps with the numerical solutions of the modified Schmid's equation, to get a χ^2 map for the termination rate parameters and the best fit k_{td}/k_{tc} value.

2. Experimental

2.1. Materials

2,2′Azobisisobutyronitrile (AIBN, K&K laboratories) was recrystallized twice from methanol (m.p. 101.5° C). Methyl methacrylate (MMA, Aldrich) was 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. The radical trap, (2-chloroethyl)benzene (T, Aldrich)and the solvent, (benzene, Aldrich) were used as received.

2.2. Polymerization

Very high molecular weight poly(methyl methacrylate) (PMMA, $M_v = 2.3 \times 10^6$) was prepared in %50 benzene solution with 0.0002gr/lt AIBN initiator. Reaction was performed in constant temperature bath at 60^oC for 336 hours. At the end of reaction polymers were precipitated from methanol and dried at reduced pressure in a vacuum oven at room temperature overnight.

2.3. Sonication

Sonication was performed in an ultrasonic bath (80W, 35kHz) at 25°C. Two identical groups of polymer solutions(12g/l polymer in benzene) were prepared and saturated with N_2 bubbling for 15mins. Radical trap was added into one group of samples. Samples with and without trap were exposed to US. Aliquots were withdrawn from each sample at specified times, precipitated with methanol and dried and their molecular weights were determined. The solution viscosity was determined by an Ubbelohde type viscometer and the mean value of five measurements was used in molecular weight determination. Molecular weight equation is given below [30]:

$$\eta = 9.39 \times 10^{-3} M_v^{0.63} \quad (4)$$

(PMMA, at25°C in methyl ethyl ketone)

3. Simulations

In the first set of experiments the concentration of the traps is sufficiently high and every chain is trapped before it has time to recombine. The evolution of the molecular weight is identical to the case where the only reaction is the chain scission. For this reason Schmid's chain scission model for concentrated solutions was taken as basis in the simulation studies. Time dependence of the number concentration polymer chains $[C]$ is given by,

$$\frac{d[C]}{dt} = [S] \tag{5a}$$

$$\frac{d[S]}{dt} = k\ln(P_{nt}/P_{n0}) \tag{5b}$$

Here $[S]$ is the number of scission events per unit time per unit volume, P_{nt} and P_{n0} are the number average degrees of polymerization at time t and at time 0. The conservation equation gives,

$$[C]P_{nt} = [C]_0 P_{n0} \tag{5c}$$

The two parameters governing this reaction are; S_0,the initial value of the chain scission rate and k, the Schmid parameter. Eq's. 5 were solved numerically by the Runge-Kutta method for different sets of the parameters S_0 and k. Simulation runs were terminated when the rate of chain breakage reached zero, corresponding to terminal molecular weight. The numerically obtained molecular weights, were compared with experimental values obtained by averaging 5 viscosimetric measurements. The χ^2 value for this set of parameters was found as the sum of the squares of the differences of the numerical and experimental molecular weights, divided by the average standart deviation of the viscometric measurements. Repetition of this process for all S_0 and k values within the scanning range, produced a complete χ^2 map.

The kinetics corresponding to natural termination involving chain scission, combination and disproportionation can be modelled by the kinetic equations,

$$\frac{d[P]}{dt} = -S\frac{[P]}{[C]} + K_a[R]^2 + 2k_{td}[R]\,[D] \tag{6a}$$

$$\frac{d[R]}{dt} = 2S\frac{[P]}{[C]} - K_b[R]^2 + 4k_{td}[D]^2 \tag{6b}$$

$$\frac{d[D]}{dt} = S\left(1 - \frac{[P]}{[C]}\right) - 2K_b[R]\,[D] - 4K_a[D]^2 \tag{6c}$$

$$\frac{d[S]}{dt} = k\ln(P_{nt}/P_{n0}) \tag{6d}$$

Here the diradicals are the chains with an active group at each end, formed by the scission of the radicals. 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. k_{td} and k_{tc} are the termination rate constants for disproportionation and combination respectively. [28] $K_a = k_{tc}/2 + k_{td}$ and $K_b = k_{tc} + k_{td}$ are constants introduced for convenience. These reactions are governed by four parameters. These are k_{tc} and k_{td}, in addition to S_0 and k define above.

The Eq's. 6 were integrated by the Runge-Kutta method. The best S_0 and k obtained in the first procedure were used without change in this part. The χ^2 for each set of the termination rate constants, k_{tc} and k_{td} were obtained by comparing the numerically obtained molecular weights with the average molecular weights for the experiments with natural termination.

All sets of termination rate parameters within the scanning range were tried in a parameter sweep and a χ^2 for each set was obtained. The χ^2 map was not plotted however as a function of k_{tc} and k_{td} but as a function of $x = log(k_{tc}/k_{td})$ and $y = log(k_{tc}^2 + k_{td}^2)$ because only the ratio of the termination rate constants is relevant for this study.

The reason for using separate data sets for each pair of parameters, instead of using the data with natural termination to obtain all parameters, was the well known ambiguity caused by obtaining four fit parameters from a single data set.

Here the definition of the rate constants adheres to the convention used by Bamford [31]. The alternate convention used by Odian [32] differs by a factor of two. However the ratios do not depend on the convention used.

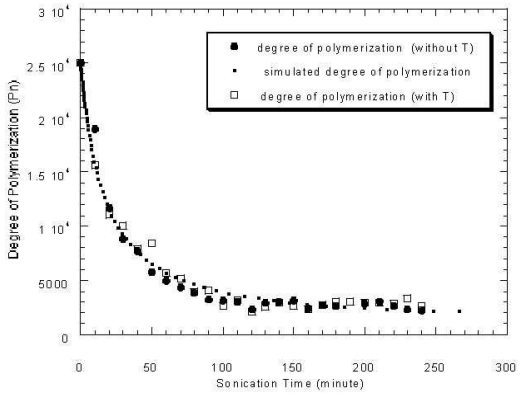

Figure 1. Viscosity average molecular weights of sonicated PMMA samples in the presence and absence of radical trap and simulated values.

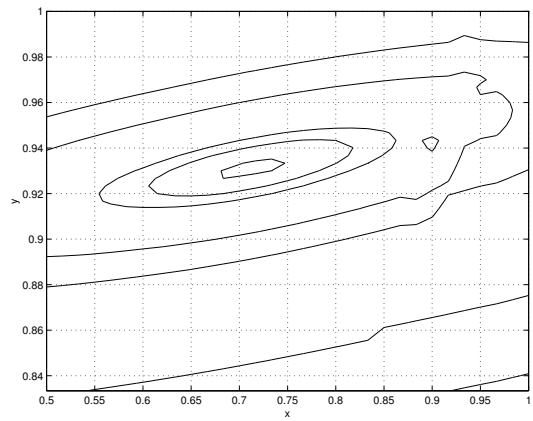

Figure 2. The χ^2 map for S_0 and k, obtained from Eq's. 5.

4. Results and Discussion

Fig. 1 shows the molecular weights of PMMA samples sonicated in the presence and absence of a radical trap. The samples terminated with trap, T, and those terminated freely, follow very similar paths. As the influence of the addition of T on the evolution of the molecular weight was small but not negligible, disproportionation is the dominant, but not the sole, termination mechanism.

The χ^2 map for S_0 and k obtained by repeating the integration of Eq's. 5 in a complete sweep is given in Fig. 2. The minimum, $X = 0.71$, $Y = 0.94$ (X and Y are defined as, $X = 1.72 \times 10^9 k$ and $Y = 3.37 \times 10^6 S_0$) corresponds to $S_0 = 2.8 \times 10^{-7}$, $k = 4.1 \times 10^{-10}$. Fig. 3 shows the χ^2 map for Eq's. 6. The x-axis is the common logarithm of the k_{td}/k_{tc} ratio. The y-axis, proportional to $\log(k_{td}^2 + k_{tc}^2)$, is not relevant for this study. The best fit $X = 0.42$ the k_{td}/k_{tc} ratio is found as 2.6 ± 0.4.

This indicates that about 28% of the chain radicals terminate by combination and the rest by disproportionation. A naive and cursory look at Fig. 1 would suggest almost all chains terminating by disproportionation, and be misleading as it would greatly underestimate the fraction of chains terminating by combination. The

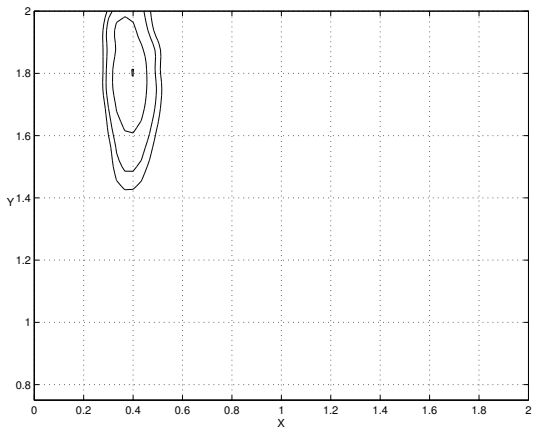

Figure 3. The χ^2 map for obtaining the k_{td}/k_{tc} ratio from Eq's. 6. $X = 0.42$ gives the k_{td}/k_{tc} as 2.6 ± 0.4

combination of macro radicals effects not only the molecular weight of the chains formed it also means that some of the chains in a sonicated sample have been broken and recombined. As a result these chains have acquired head to head bonds in their backbones which alter their mechanical properties.

Bevington *et al.* [20] had found, by the labelled initiator method, that the k_{td}/k_{tc} ratio depends on the temperature. At 25°C it is 2.13 and at 60°C it is 5.75. Our result matched their result at room temperature. Previous results on the k_{td}/k_{tc} ratios of poly (styrene) and poly (ethyl methacrylate) in sonochemical environments [28] were also consistent with the results in polymerization environments. However further studies are needed to claim that termination in sonochemical and reaction environments are similar.

As the scission takes place preferentially at the middle [5, 6], 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 [33]. These results show that breaking the polymer chain by US is a simple, straightforward and reliable method for determining the k_{td}/k_{tc} in a sonochemical environment and comparison of experimental results with simulations is seen to be very useful in interpreting the results.

5. Acknowledgements

The financial support of ITU Research Fund (Graduate School) is acknowledged.

References

[1] G. J. Price, Adv. in Sonochem., **1**, 231 (1990).
[2] G. Madras, S.Kumar, S. Chattopadhyay, Polym. Degrad. and Stab., **69**, 73 (2000).
[3] G. Madras, S. Chattopadhyay, Polym. Degrad. and Stab., **71**, 273 (2001).
[4] G. Madras, V. Karmore, Polym. Int., **50**, 683 (2001).
[5] K. S. Suslick, (Ed), *Ultrasound. Its Chemical, Physical and Biological Effects*, VCH publishers, New York (1988).
[6] T. J. Mason and J. P. Lorimer, *Sonochemistry. Theory, Applications and Uses of Ultrasound in chemistry*, Ellis Harwood Limited, John Wiley & Sons, New York (1988).
[7] M. S. Doulah, J. App. Polym. Sci., **22**, 1735 (1978).
[8] A. Giz, H. Çatalgil-Giz, M. Sunar, Macromol. Theory and Sim., **10**, 117 (2001).
[9] P. A. R. Glynn, B. M. E. Van der Hoff, P. M. Reilly, J. Macromol. Sci. Chem., **A6**, 1653 (1972).
[10] P. A. R. Glynn, B. M. E. Van der Hoff, P. M. Reilly, J. Macromol. Sci. Chem., **A7**, 1695 (1973).
[11] G. Schmid, Phys. Z., **41**, 326 (1940).
[12] G. Schmid, Z. Phys. Chem., **A186**, 113 (1940).
[13] P. Cacioli, G. Moad, A. K. Serelis and D. H. Solomon, Polym. Bull. (Berlin), **11**, 325 (1984).
[14] T. Kashiwagi, A. Inaba, J. E. Brown, K. Hatada, T. Kitayama and E. Masuda, Macromolecules, **19**, 2160 (1986).
[15] A. Meisters, G. Moad, E. Rizzardo and D. H. Solomon, Polym. Bull(Berlin), **20**, 499 (1988).
[16] L. E. Manring, Macromolecules, **22**, 2673 (1989).
[17] C. H. Bamford and E. F. T. White, Trans. Faraday Soc, **54**, 268 (1958).
[18] S. Bizilj, D. P. Kelly, A. K. Serelis, D. H. Solomon and K. E. White, Aust. J. Chem., **38**, 1657 (1985).
[19] P. Cacioli, D. G. Hawthorne, R. L. Laslett, E. Rizzardo and D. H. Solomon, Macromol. Sci and Chem., **A23**, 839 (1986).
[20] J. C. Bevington, H. W. Melville and R. P. Taylor, J. Polym. Sci., **14**, 463 (1954).
[21] G. Ayrey and C. G. Moore, J. Polym. Sci., **36**, 41, (1959).
[22] G. V. Schulz, G. Henrici-Olivé and S. Olivé, Makromol. Chem., **31**, 88 (1959).
[23] C. H. Bamford and A. D. Jenkins, Nature (London) **176**, 78 (1955).
[24] C. H. Bamford, A. D. Jenkins and R. Johnston, Trans. Faraday Soc., **55**, 179 (1959).
[25] P. W. Allen, A. G. Ayrey and C. G. Moore, J. Polym. Sci, **36**, 55 (1959).
[26] G. M. Burnett and A. M. North, Makromol. Chem., **60**, 960 (1964).
[27] N. Erolan, F. Arısan, and H. Çatalgil-Giz, Angew. Makromol. Chem., **226**, 53 (1995).
[28] H. Çatalgil-Giz, A. Giz and A. Öncül-Koç, Polym. Bull. **43**, 215 (1999).
[29] G. Schmidt-Naake, M. Drache, M. Weber, Macromol. Chem. Phys., **203**, 2232 (2002).
[30] J. Brandrup, A. H. Immergut and E. A. Grulke, Ed., Polymer Handbook, VII, 11(46) (1999).
[31] C. H. Bamford, *Radical Polymerization*, Encyclopedia of Polymer Science and Engineering, **13**, 708, Wiley-Interscience, New York, (1991).
[32] G. Odian, *Principles of Polymerization, 3rd Ed.*, Wiley- Interscience, New York (1991).
[33] T. Kashiwagi, A. Inaba and E. Brown, Macromolecules, **19**, 2160 (1986).