

## Ultrasonic Degradation Studies of Polyacrylates

<sup>1</sup>FARAH KANWAL\*, <sup>2</sup>RICHARD A. PETHRICK AND <sup>3</sup>TAHIR JAMIL

<sup>1</sup>*Institute of Chemistry, University of the Punjab, Lahore, Pakistan.*

<sup>2</sup>*Department of Pure and Applied Chemistry, University of Strathclyde,  
Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL, UK.*

<sup>3</sup>*Institute of Chemical Engineering, University of the Punjab, Lahore, Pakistan.*

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**Summary:** Ultrasonic degradation studies of poly(methylmethacrylate; PMMA) and poly(butyl methacrylate; PBMA) in solutions are reported. Measurements of the molar mass distribution using gel permeation chromatography indicate very little evidence of degradation for shorter chain PMMA. For the higher molar mass PBMA, a progressive decrease in the number and weight average molar mass was observed. The molar mass distribution progressively narrowed with increase in ultrasonic irradiation time. A decrease in viscosity of PBMA solution was also observed with increasing irradiation time. The results show that there is limiting molar mass below which significant ultrasonic degradation is not possible at the applied frequency of 20 kHz.

### Introduction

Poly(methyl methacrylate; PMMA) has been used by many workers [1-3] to investigate radiation induced degradation, photochemical, mechanical and thermal decomposition. This polymer undergoes cleavage of backbone and depolymerisation to monomer when heated [4, 5]. Schoon and Rieber [6, 7] studied the degradation of many different polymers in an attempt to correlate the limiting molecular weight with the nature of the polymer. It was found that under the same condition, chemically different polymer gave the same result and therefore the chemical nature of the polymer is relatively unimportant. Malhotra [8] reported degradation of a series of alkyl methacrylate with the alkyl side chain ranging between methyl and octadecyl. It was suggested that the chain structure and molecular weight were the important factors in determining the kinetics of degradation rather than the bulk size of the substituent. Wu *et al.*, [3] reported ultrasonic degradation on samples of poly(methyl methacrylate) with different molecular weight distributions. The extent of degradation was measured from molecular weight distribution by using gel permeation chromatography (GPC). The polydispersity decreased as a function of irradiation time for polymers with an initial broad mass distribution. For polymers with an initial narrow mass distribution, polydispersity increased initially, passed through a maximum and then gradually decreased.

A variety of different theoretical models have been proposed by Price *et al.* [9], Weissler [10], and Brett *et al.* [11]. These models attempt to explain the influence of factors such as frequency and intensity of radiation, solvent, temperature, nature of dissolved gas, external pressure and the molecular mass distribution on the rate and molar mass of the degraded species. Doulah [12] has proposed that the shock wave energy released as the cavity collapses is responsible for the degradation process. However this theory does not intuitively predict the lower limit in molar mass for degradation or the scissions at the center of the chain. In our previous studies [13] observed a correlation between the rate of ultrasonic degradation and the predictions of the ability of the polymer solution to absorb energy through the polymer chain motions. The correlation would predict that the rate of degradation should primarily be controlled by the initial molar mass of the polymer and its size in solution. Sterling *et al.*, [14] and Madras *et al.*, [15-17] have attempted to calculate the rate of the degradation process based on various assumptions. If the degradation process is assumed to occur via thermolytic reaction kinetics then it is possible to calculate the expected distribution of molar mass of polymers that will result. Bond scission, occurring either randomly along a chain backbone or at the chain end is considered to be the major reaction process in polymer thermolysis. Under

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\*To whom all correspondence should be addressed.

lying this bond scission are free radical mechanisms, including initiation and termination, hydrogen abstraction, and beta scission. Population-balance equations for the molecular weight distributions of macromolecules or their radicals describe the dynamics of the reactions. The governing integro-differential equations for continuous distributions can be solved by moment methods, similarity techniques, other analytical procedures, or numerical methods. This theory does not however explain the observation of a limiting lower molar mass weight for degradation of the polymer chain. Madras and McCoy [15] has pointed out that the ultrasonic degradation of polymers is distinguished from thermal degradation by scission taking place at the midpoint rather than as a random event down the length of the polymer chain.

In this study two samples shorter chain poly(methyle methacrylate) and one sample of high molar mass poly(butyle methacrylate) were used for degradation studies by ultrasonic radiation. The aim of the study was to explore whether a lower molar mass degradation exists for chemically different polymers and also to determine the range of lower limiting molar mass.

### Results and Discussion

For PMMA (I) the values of Mw and Mn of the solution for 200 min irradiation did not show (Fig. 1) any significant change within experimental error. For PMMA (II) similar behavior was observed. But under similar experimental conditions polystyrene with initial molar mass of  $3.1 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$  had shown significant degradation [13]. Thomas (18) had studied high molar mass poly(methyle metharylate), polystyrene and poly-butene and found that the rate of degradation is similar irrespective of the chemical nature. A high molar mass sample of ploy(butyl-methyl methacrylate) was also subjected to ultrasonic irradiation for the same period of time and a marked drop in the number and weight average molar mass with irradiation time was observed (Fig. 1). Molar mass decreases rapidly in first hour and then slows down (Fig. 1). Therefore, these changes are associated with the lower limit of molar mass. The molar mass distribution (polydispersity) below  $10^5 \text{ g}\cdot\text{mol}^{-1}$  for PMMA appears to be unchanged (Fig. 2). The main changes in the distribution occurred above  $10^5 \text{ g}\cdot\text{mol}^{-1}$  which is in line with the work reported by Kanwal *et al.* [13, 19]. The consequence of the scission of chains with molar masses in the range of

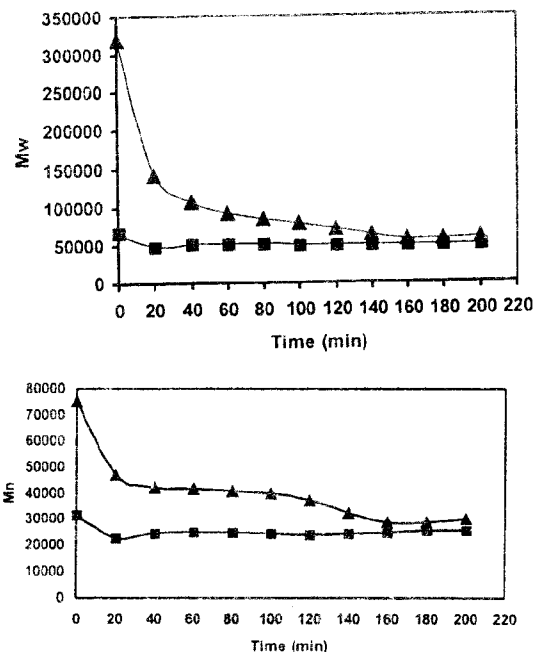


Fig. 1: Variation of Mw and Mn as a function of irradiation time for 2 % w/v solution of PBMA (▲) and PMMA (■) in toluene at  $20 \pm 1^\circ\text{C}$ .

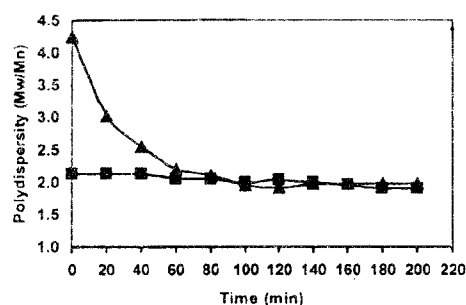


Fig. 2: Variation of polydispersity (Mw/ Mn) as a function of radiation time for a 2 % w/ v PBMA (▲) and PMMA (■) in toluene at  $20 \pm 1^\circ\text{C}$ .

$10^4$  to  $10^5 \text{ g}\cdot\text{mol}^{-1}$  leads to the significant narrowing of the molar mass distribution. The products of degradation are known to be free radicals in the case of poly(methyle methacrylate) and poly(butyle methacrylate). The primary radicals are formed by the homolytic cleavage of the PMMA and PBMA backbone. Tabata *et al.*, [4] and Zulfiqar *et al.*, (5) have also suggested the possibility of production of secondary radicals. These radicals can initiate further

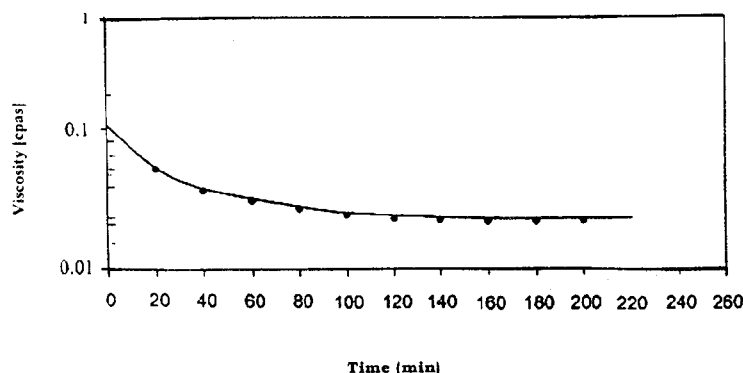


Fig. 3: Variation of viscosity as a function of irradiation time at  $20 \pm 1$  °C for 2 % w/ v PBMA in toluene.

linkage in a polymer-polymer or polymer-monomer system during ultrasonic irradiation.

The change in the viscosity of PBMA in toluene was also monitored as a function of irradiation time (Fig. 3). For all the solutions, the effect of ultrasonic irradiation process is to produce a limiting molecular weight that leads to the convergence of final solution viscosity.

#### Theoretical Modeling

The theoretical modeling [13, 19-21] is used to calculate the variation of loss modulus and viscosity for Poly(methyle methacrylate) and poly (butyl methacrylate). The variation of  $\eta(\omega)$  and  $G''$  with frequency (Fig. 4), were calculated using data from Fig. 1 and Fig. 3. The model relate the absorption frequency with molar mass interms of energy absorption; the first normal mode dissipates approximately two thirds of the total energy absorbed by the polymer molecules and is associated with an elongation of the polymer molecule in the flow direction. The first normal mode, according to Sivalingam *et al.*, [22], corresponds to a motion of the chain in which the two ends are moving in opposite directions and a node exists at the center. The node will correspond to a high stress region and would be the favored location for chain scission. Once the chain length has been degraded to a point at which its first normal mode is approximately a decade above that of the irradiation frequency, little coupling between the perturbation in solution and the polymer will occur.

From Fig. 4, variation of loss modulus at 20 kHz as a function of time was calculated and is

plotted in Fig. 5. It is apparent from Fig. 5 that as the degradation proceed, the loss modulus which is directly proportional to the absorption of the ultrasound radiation also decreases. It is also noticeable that just as with the viscosity, the loss-acoustic absorption also tends towards a constant value for the species that undergo degradation. This signifies a correlation between the normal mode relaxation behavior and the processes involved in the degradation.

The ultrasonic degradation study of poly (methyle methacrylate) and Poly(butyle methacrylate) shows that there is correlation between the lower limiting molecular weight for degradation and the loss of effective viscoelastic absorption mechanisms. This is predicted by the calculation presented earlier [13, 19]. The lower molar mass (below  $M_w$  70,000  $\text{g}\cdot\text{mol}^{-1}$ ) poly(methyle methacrylate) samples do not exhibit any significant degradation while the high molar mass poly(butyl methacrylate) shows clear degradation. These facts further certify that there is a lower limiting molar mass below which no degradation is possible [15]. The theoretical models of polymer degradation [14-17] incorporated this limit but have not given any explanation. The prediction of the limiting molar mass can be made through the viscoelastic model and the values are function of concentration, solvent, temperature and polymer type, consistent with experimental observation [16]. The connection between the ability to degrade a polymer by ultrasound and the decrease in viscosity of the solution has been already recognized [17]. The experimental results of PMMA and PBMA gives further evidence that the connection between the observation of a limiting lower molar mass for

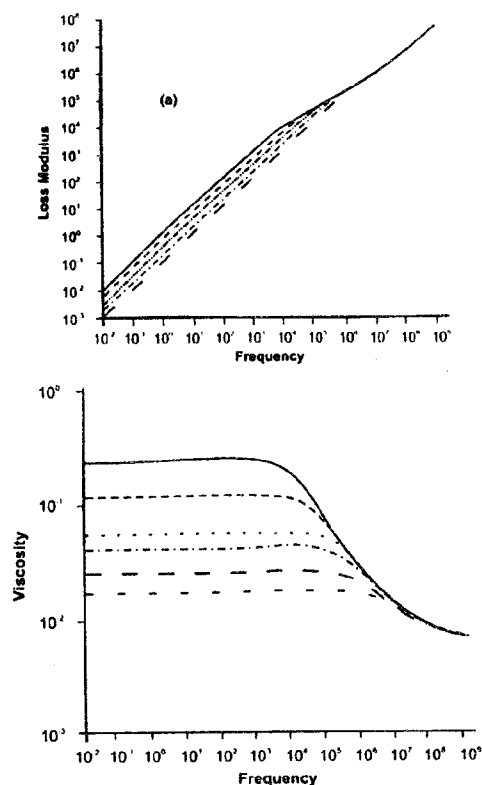


Fig. 4. Variation of the (a) loss modulus and (b) viscosity as a function of frequency at  $20 \pm 1^\circ\text{C}$  for a 2% w/v solution of PBMA in toluene. Curves calculated from the gel permeation chromatography data using the Wang Zimm theory. Key : (—) time = 0min, (---) time = 40min, (- - -) time = 80min, (· · ·) time = 120 min, (- - - -) time = 160min, (- - -) time = 200min.

degradation and the ability to absorb energy through viscoelastic deformation is probably correct [19].

## Experimental

### Materials

The PMMA and PBMA were purchased from Aldrich chemicals U.K. The weight average mole-

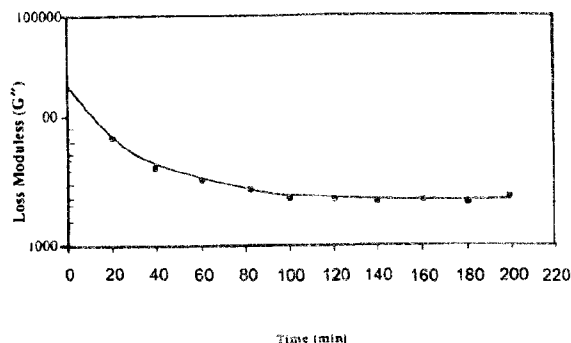


Fig. 5: Variation of the calculated loss modulus for the solution of PBMA as a function of irradiation time.

cular weight and polydispersity of the two PMMA and PBMA samples were determined by GPC analysis and are given in Table-1. Solutions of PMMA and PBMA were prepared in analytical grade toluene.

### Ultrasonic Degradation

For degradation studies, solutions of two samples of PMMA and one sample of PBMA were prepared by dissolving 2 gm of the polymers in 100 ml of analar grade toluene. Ultrasonic degradation of these solutions was carried out using a Lucas Dawes Ltd sonicator model 250. The sonicator is capable of delivering 200 watts at a frequency of 20 KHz and has a duty cycle variable between 10 and 90 %. The solution was contained in a thermostatted double wall cell of 300 ml capacity maintained at a constant temperature during the experiment. The irradiation was monitored for 200 minutes and the temperature was maintained at  $20.0 \pm 0.5^\circ\text{C}$ . During the irradiation experiment, 2 ml aliquots of reaction mixture was withdrawn at 20 minutes intervals and diluted to 1 % for subsequent viscosity and gel permeation chromatographic analysis.

### Gel Permeation Chromatography

The polymer molecular mass and its distribution were obtained using a Polymer Labs. PLGEL 100 micrometer type gel permeation chroma-

Table-1: Molar Mass information of polymers

Polymer	Weight average molar mass (g/mole)	Polydispersity (Mw/Mn)
Poly(methylmethacrylate) (PMMA-I)	$6.7 \times 10^4$	2.13
Poly(methylmethacrylate) (PMMA-II)	$6.4 \times 10^4$	2.15
Poly (butylmethacrylate) (PBMA)	$3 \times 10^5$	4.26

tograph equipped with a refractive index detector. The columns were calibrated using polystyrene standards ranging from  $10^3$ - $10^6$ . Analysis of the intensity elution curves and calculation of the resultant molar mass distribution were performed using a data analysis system.

#### Viscosity measurement

Viscosity was obtained by using an Ostwald's viscometer thermostatted in a water bath at  $25.0 \pm 0.5^\circ\text{C}$ . Flow time of the solution was compared with that of the solvent to measure the viscosity. The intrinsic viscosity of the solutions was calculated by extrapolating the viscosity as a function of concentration to zero concentration.

#### Conclusions

The data presented in this paper indicates the existence of a limiting molar mass below which no degradation or significant degradation can be possible. The value of the limiting molar mass is dependent on the frequency of the ultrasonic used and to some extent on the amount of entanglements present in the molecular chain but not on the chemical nature of the polymer. We believe that the cavity collapse idea for ultrasonic degradation don't hold as the lower molar mass have not shown any degradation. The limiting molecular weight can therefore be predicted according to the normal mode relaxation theory. The concept that the normal mode process is connected with the degradation process is also consistent with the most probable site for scission being at the centre of the chain and produces macro-radicals that can be used to produce copolymers.

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#### Reference

1. S. L. Malhotra and J. M. Gathuer, *Macromol Sci.*, **A(18)**, 78 (1982).
2. G. Schmid, C. Schneider, A. Hengglin and Z. Kolloid, **148**, 73 (1956).
3. C. B. Wu, P. J. Sheth and J. F. Jhonson, *Polymer.*, **18**, 822 (1977).
4. M. Tabata and J. Shoma, *J. Polym. Sci.*, **16**, 589 (1980).
5. S. Zulfiqar, M. Zulfiqar, M. Naway, I. C. McNiell and J. G. Gorman, *Polymer Degradation and Stability.*, **30**, 195 (1990).
6. T. G. Schoon and G. A. Rieber, *Makromol Chem.*, **23**, 43 (1972).
7. T. G. Schoon and G. A. Rieber, *Makromol Chem.*, **15**, 263 (1971).
8. S. L. Malhotra, *J. Macromol Sci. Chem.*, **A23(6)**, 72 (1986).
9. G. J. Price, P. S. Smith, *Polymer*, **34**, 4111 (1993).
10. A. Weissler, *J Appl Phys.*, **21**, 171 (1950).
11. A. W. Brett and H. H. G. Jellinek, *J Polym. Sci.*, **13**, 111 (1954).
12. M. S. Doulah, *J Apply Polym. Sci.*, **22**, 1735 (1978).
13. F. Kanwal, J. J. Liggat and R. A. Pethrick, *Polym. Degrad. Stab.*, **68**, 445 (2000).
14. W. J. Sterling, B. J. McCoy, *AIChE. Journal.*, **47**, 2289 (2001).
15. G. Madras and B. J. McCoy, *AIChE. Journal.*, **47**, 2341 (2001).
16. G. Madras and V. Karmore, *Polym. Int.*, **50**, 683 (2001).
17. G. Madras and S. Chattopadhyay, *Polym Degrad. Stab.*, **71**, 273 (2001).
18. G. R. Thomas, *J. Phys. Chem.*, **63**, 1725 (1959).
19. F. Kanwal and R. A. Pethrick, *Polym Degrad Stab.*, **84**, 1 (2004).
20. F. W. Wang and B. H. Zimm, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1619 (1974).
21. F. W. Wang and B. H. Zimm, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1639 (1974).
22. G. Sivalingam, Agarwal, Nitin, Madras and Giridhar, *AIChE. Journal.*, **50**, 2258 (2004).