



Kinetics of the ultrasonic degradation of poly (alkyl methacrylates)

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ARTICLE INFO

Article history:

Received 29 April 2008

Received in revised form 15 July 2008

Accepted 31 August 2008

Available online 11 September 2008

Keywords:

Ultrasound

Degradation

Poly (alkyl methacrylate)s

Initiator

Continuous distribution kinetics

ABSTRACT

The influence of the alkyl group substituents on the ultrasonic degradation of poly (alkyl methacrylate)s, namely poly (methyl methacrylate) (PMMA), poly (ethyl methacrylate) (PEMA) and poly (butyl methacrylate) (PBMA) was studied. The rate coefficient increased with an increase in the number of carbon atoms in the alkyl group: thus the order of degradation was PBMA > PEMA > PMMA. This was attributed to the scission of the main chain, which increases with the length of the side chain. The ultrasonic degradation of PBMA was investigated in various solvents, at different temperatures and at different ultrasound intensities. The degradation rate coefficients increased logarithmically with the decrease in vapor pressure and increased linearly with an increase in viscosity of the solvent and ultrasound intensity. The effect of three different initiators, benzoyl peroxide (BPO), dicumyl peroxide (DCP) and azo-bisobutyronitrile (AIBN) on the ultrasonic degradation of PBMA was also studied. The degradation of the polymer decreased in the presence of the initiator. A continuous distribution model was developed for the radical mechanism involved in degradation and was used to determine the degradation rate coefficients of PBMA in presence of initiator. The model indicated that the degradation rate coefficient of the interaction of the PBMA radical with the initiator is independent of the dissociation constant of the initiator.

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1. Introduction

Among several methods used for degrading polymers like thermal, mechanical, radiative, chemical, biological, etc., the ultrasonic assisted degradation of polymers is the among the fastest. When an ultrasonic wave passes through the polymer solution, it produces cyclic tensions and compressions causing cavitation. The microbubbles formed during cavitation are the main cause for degradation of the polymer [1–6]. Microbubbles collapse and produce intense shear and shock waves on the polymer molecules near the bubble. Because of this high shear polymer molecules near the collapsing microbubble move faster than the polymer molecules far from the cavitation. Due to this relative motion of polymer chains and mechanical stress generated, the polymer chain breaks almost at the mid-point [3,7]. The molecular weight decreases continuously till it reaches a limiting molecular weight [3].

The effect of various parameters such as vapor pressure [8–13], initial molecular weight [9], temperature [10,14], pH [13], concentration [8,13,15] and viscosity [10,16] on the ultrasonic degradation of polymers has been investigated. The ultrasonic degradation of many polymers such as dextran [5], poly (alkyl acrylates) [10], polyacrylamide [14], poly (methyl methacrylate)

[16], polyvinylacetate [17], polyethyleneoxide [14,18], poly (ethylene adipate) [18], poly (dimethylsiloxane) [18], polybutadiene [19], polypropylene [19] and polystyrene [20] has been studied. Initiator plays an important role in both polymerization and degradation of polymers [17,21–25]. The previous studies on the ultrasonic degradation of polymers have been summarized in literature reviews [3,26].

There is a considerable interest on the thermal decomposition of poly (methacrylic esters) and a number of studies have reported the thermal degradation (by pyrolysis) of these polymers [27–30]. The degradation of these polymers in solution would have several advantages like better heat transfer and uniform temperature distribution compared to that of thermal degradation by pyrolysis. Thus thermal degradation of PMMA has been investigated in solution [16,31,32]. The effect of solvent on the ultrasonic degradation of PMMA was studied and correlated to the vapor pressure of the solvent and kinematic viscosity of the solution and polymer-solvent interaction parameters [16]. Recently the effect of alkyl group on thermal degradation of poly (alkyl methacrylate)s in supercritical fluids has been determined [33]. The degradation of poly (alkyl methacrylate)s under SF₅⁺ primary ion bombardment using time of flight secondary ion mass spectroscopy has been also investigated [34].

In this study, we have investigated the effect of three radical generators namely benzoyl peroxide (BPO), dicumyl peroxide (DCP) and azo-bisobutyronitrile (AIBN) on the ultrasonic degradation of PBMA. Because these compounds are used as radical ini-

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tiators in polymerization, these are referred to as initiators in this study.

This is the first study that investigates the effect of alkyl group on the ultrasonic degradation of poly (alkyl methacrylates) and the effect of solvent, temperature, intensity and initiator on the degradation of PBMA. A new continuous distribution model has been developed to determine the degradation rate coefficients. The model indicates the rate coefficient of the interaction of the PBMA radical with the initiator is independent of the initiator dissociation constant.

2. Materials

Methyl methacrylate, poly (ethyl methacrylate) (initial molecular weight, $M_{n0} = 112,000$; polydispersity, $PD = 1.8$), poly (isopropyl methacrylate) ($M_{n0} = 90,000$; $PD = 1.6$) and poly (butyl methacrylate) ($M_{n0} = 98,000$; $PD = 1.5$) were purchased from Sigma–Aldrich. Poly (methyl methacrylate) ($M_{n0} = 176,000$; $PD = 1.7$) was synthesized by bulk polymerization technique with benzoyl peroxide as the initiator at 60 °C. The solvents tetrahydrofuran, chlorobenzene, *o*-dichlorobenzene, toluene, benzene and *o*-xylene were purchased from S.D. Fine Chemicals (India). The solvents were distilled and filtered through 0.22 μm nylon filter paper before use. The radical generators (initiators), azo-bisobutyronitrile (AIBN), benzoylperoxide (BPO) and dicumylperoxide (DCP) were purchased from S.D. Fine Chemicals, Rolex, and N.R. Chemicals, respectively.

2.1. Degradation experiments

About two gram per liter of polymer solutions were prepared and 50 mL solution in various solvents was taken in a 100 mL glass beaker. Horn-type ultrasonic processor (Vibronics, India) with an intensity 36 W cm^{-2} and frequency 25 kHz was used for degradation process. Experiments were conducted by varying the intensity from 16 to 36 W cm^{-2} and temperature from 30 to 60 °C. The temperature of the polymer solution was maintained at the desired temperature (± 1 °C) using a thermostated water bath. Further details of the experimental setup can be found elsewhere [13,14].

Samples of 0.5 mL were collected at various time intervals for analysis by gel permeation chromatography (GPC). The limiting molecular weight (MW) was obtained by conducting experiments for 10 h, when the molecular weight reaches a constant value of 40,000. Multiple experiments indicated that the error in rate coefficient is approximately 3%.

2.2. Gel permeation chromatography analysis

The samples were analyzed in gel permeation chromatography. The system consists of a high pressure liquid chromatography (HPLC) pump (Waters 515) for pumping the eluent, THF at a flow rate of 1 mL/min, Rheodyne (7725i) injector, three size exclusion columns packed with crosslinked poly (styrene-divinyl benzene) (Styragel HR-5E, 4, 1) maintained at 50 °C. A differential refractive index detector (Waters RI 2410) was used for detection and stored using a data acquisition system. The chromatograph was converted to molecular weight distribution using a universal calibration based on polystyrene standards (Polymer Lab, UK). The same universal calibration curve was used for all the three polymers. Multiple analyses to determine the molecular weight of the same sample indicated the error was less than 1%.

2.3. Initiator degradation rate

The dissociation rate coefficient of the initiators in presence of ultrasound was determined using the same equipment under the

same experimental conditions. The experiments were conducted for several hours and the concentration of the initiators, AIBN, BPO and DCP was determined by high pressure liquid chromatography (HPLC). 20% (v/v) water and 80% (v/v) methanol was used as eluent at 0.5 mL/min. The absorbance was continuously monitored using a UV detector at 340, 235 and 288 nm for AIBN, BPO and DCP, respectively. The system was calibrated with known concentration samples. Based on the time evolution of the concentration, it was found that the dissociation rate was first-order. The dissociation constants ($k_d \times 10^3$) of AIBN, BPO and DCP in ultrasound were determined to be 13, 9 and 3.7 min^{-1} , respectively. These dissociation rate constants are comparable to that ($2-4 \times 10^{-3} \text{min}^{-1}$) obtained at 70 °C thermally. This indicates the enhancement of degradation of the initiators in ultrasound compared to the degradation obtained thermally. Further, no degradation of the polymers occurs at ambient conditions in absence of ultrasound indicating the enhancement observed with ultrasound.

2.4. Theoretical model

The model developed using continuous distribution kinetics was used to determine the rate coefficient for the ultrasonic degradation of polymer. Though the proposed radical mechanism for polymer degradation discussed below is new, it builds upon the existing models that discuss ultrasonic degradation in the absence [13,14] of and in the presence of initiators [10]

$$P(x) \xrightleftharpoons[k_t]{k_i} R^*(x') + R^*(x - x') \quad (1)$$

$$P(x) \xrightleftharpoons[k_{Ht}]{k_{Hr}} R^*(x) \quad (2)$$

$$R^*(x) \xrightarrow{k_s} P(x') + R^*(x - x') \quad (3)$$



$$R^*(x) + D_2 \xrightarrow{k_{Dp}} P(x) + D^* + DH \quad (5)$$

The initiation and termination steps are represented by Eq. (1). $P(x)$ represents the polymer molecule with molecular weight x and R^* represents the radical formed after fission. According to the long-chain approximation (LCA) the initiation and the termination rates are assumed to be zero [35]. The LCA is based on the insignificant effect of initiation and termination reactions compared to the predominant influence of the depropagation reactions. This assumption is based on the relatively insignificant magnitude of the thermally induced initiation rate because of the high activation energy and the low probability of bimolecular addition reactions (termination) between radicals at small concentrations. Hydrogen abstraction and the depropagation reaction of the polymer are represented by Eqs. (2) and (3), respectively. The initiator undergoes cleavage and produces free radicals, as given by reaction (4). Reaction (5) represents the formation of stable polymer by the interaction of the polymer radical with the initiator. Because the initiator does not influence the scission of the polymer, Eq. (1), the overall degradation is non-random both in the presence and in the absence of the initiator. Thus, the molecular weight distributions obtained in both cases are similar and do not indicate random chain scission.

An additional reaction where $P(x)$ can react with D^* to yield radicals can be included but this will result in more scission in presence of an initiator. However, the experimental data indicates that the degradation rate actually decreases in the presence of the initiator and thus the initiator acts as a capping agent for the radicals.

$p(x, t)$ and $D(t)$ represent the molar concentrations of polymer, $P(x)$ and initiator, D_2 . The population balance equations for the var-

iation of the concentrations of the polymer $p(x, t)$, polymer radical $r(x, t)$ and initiator $D(t)$ are [10,11,35]

$$\frac{\partial p(x, t)}{\partial t} = -k_h(x)p(x, t) + k_H(x)r(x, t) + k_D(x)r(x, t)D(t) + \int_x^\infty k_s(x')\Omega(x, x')r(x', t)dx' \quad (6)$$

$$\frac{\partial r(x, t)}{\partial t} = k_h(x)p(x, t) - k_H(x)r(x, t) - k_D(x)r(x, t)D(t) - k_s(x)r(x, t) + \int_x^\infty k_s(x')\Omega(x, x')r(x', t)dx' \quad (7)$$

$$\frac{dD(t)}{dt} = -k_d(x)D(t) - \int_0^\infty k_D(x)D(t)r(x, t)dx \quad (8)$$

In this model the stoichiometric kernel is taken as a Dirac delta function $\Omega(x, x') = \delta[x - \frac{x'}{2}]$, which allows a distribution at the midpoint of the polymer chain [9,10,17]. The rate coefficients $k_h(x)$ and $k_H(x)$ are assumed to be independent of molecular weight because the hydrogen abstraction does not depend on the polymer chain length [17]. When the polymer reaches the limiting molecular weight (x_l), the degradation should be zero. Therefore, the rate coefficient [9] is represented as $k_s(x) = k_s(x - x_l)$. $k_D(x)$ is assumed to be independent of molecular weight, i.e., $k_D(x) = k_D$.

Applying moment operation $p^{(j)}(t) = \int_0^\infty p(x, t)x^j dx$ for Eqs. (6)–(8)

$$\frac{dp^{(j)}(t)}{dt} = -k_h p^{(j)}(t) + k_H r^{(j)}(t) + k_D r^{(j)}(x, t)D(t) + \frac{k_s}{2^j} (r^{(j+1)}(t) - x_l r^{(j)}(t)) \quad (9)$$

$$\frac{dr^{(j)}(t)}{dt} = k_h p^{(j)}(t) - k_H r^{(j)}(t) - k_D r^{(j)}(x, t)D(t) - k_s (r^{(j+1)}(t) - x_l r^{(j)}(t)) + \frac{k_s}{2^j} (r^{(j+1)}(t) - x_l r^{(j)}(t)) \quad (10)$$

$$\frac{dD(t)}{dt} = -D(t)(k_d + k_D r^{(0)}) \quad (11)$$

The initial conditions for the equations are $p^{(j)}(t=0) = p_0^{(j)}$ and $r^{(j)}(t=0) = 0$. Applying Quasi-steady-state approximation (QSSA), i.e., the rate of formation of radicals is approximately equal to the rate of loss of radicals [35]. The basis of the QSSA is the small number of radicals and therefore the negligible change of the radical concentration with time as compared to the time variation of the polymer concentration

$$\frac{dr^{(j)}(t)}{dt} = 0 \quad (12)$$

$$r^{(0)}(t) = \frac{k_h}{(k_H + k_D D(t))} p^{(0)}(t) \quad (13)$$

$$r^{(1)}(t) = \frac{k_h p^{(1)} - \frac{k_s}{2} r^{(2)}(t)}{(k_D D(t) + k_H - \frac{k_s}{2} x_l)} \quad (14)$$

$j = 0, 1$ and 2 corresponds to the zeroth, first and second moments, respectively. The rate of change of mass concentration is zero, $\frac{dp^{(1)}(t)}{dt} = 0$, $p^{(1)}(t) = p_0^{(1)}$ indicating mass conservation. The rate of change of the molar concentration of polymer is

$$\frac{dp^{(0)}(t)}{dt} = -k_h p^{(0)}(t) + k_H r^{(0)}(t) + k_D r^{(0)}(x, t)D(t) + k_s (r^{(1)}(t) - x_l r^{(0)}(t)) \quad (15)$$

Defining, $k_1 = \frac{k_h k_h}{k_H}$; $k_2 = \frac{k_D}{k_H}$, Eqs. (4) and (15) become

$$\frac{dD(t)}{dt} = -k_d D(t) \left(1 + \frac{k_h k_2 p^{(0)}}{k_d (k_2 D(t) + 1)} \right) \quad (16)$$

$$\frac{dp^{(0)}(t)}{dt} = \frac{-k_1 x_l p^{(0)}(t)}{(1 + k_2 D(t))} + \frac{k_1 p^{(1)}(t) - \frac{k_s^2}{2k_H} r^{(2)}}{(1 + k_2 D(t) - \frac{k_s x_l}{2k_H})} \quad (17)$$

As $t \rightarrow \infty$, $M_n \rightarrow x_l$, implying $\frac{x_l k_s}{2k_H} \ll 1$. From previous studies [36], $k_h \approx 10^{-2} \ll 1$. As $\frac{x_l k_s}{2k_H} = \frac{x_l k_1}{2k_H}$ and k_1 is 10^{-8} (as determined experimentally in this study), $x_l = 40,000$, this approximation is valid. Further, $p^{(0)}$ is 10^{-5} , k_d is between 10^{-2} and 10^{-3} (as determined experimentally in this study) and k_2 is 130 (as determined later in this study), $k_h k_2 p^{(0)}/k_d \ll 1$, thus Eq. (16) becomes

$$\frac{dD(t)}{dt} = -k_d D(t) \quad (18)$$

Solving Eq. (18) with the initial condition, $D(t=0) = D_0$, the initial concentration of the initiator

$$D(t) = D_0 \exp(-k_d t) \quad (19)$$

$$\frac{dp^{(0)}(t)}{dt} = \frac{k_1 (p^{(1)} - x_l p^{(0)}(t))}{(1 + k_2 D(t))} \quad (20)$$

Eq. (19) is substituted into Eq. (20) and solved with the initial condition $p^{(0)}(t=0) = p_0^{(0)}$

$$\ln(Y) = \frac{k_1 x_l}{k_d} \ln \left(\frac{e^{(k_d t)} + k_2 D_0}{1 + k_2 D_0} \right) \quad (21)$$

where $Y = \frac{(\frac{1}{M_{n0}} - \frac{1}{x_l})}{(\frac{1}{M_n} - \frac{1}{x_l})}$; $M_n = \frac{p_0^{(1)}}{p^{(0)}}$

In the absence of initiator, $D_0 = 0$, Eq. (21) reduces to

$$\ln(Y) = k_1 x_l t \quad (22)$$

This equation is exactly the same as obtained before for the ultrasonic degradation of polymers without initiator [13,14,36].

3. Results and discussion

The effect of alkyl group on the ultrasonic degradation of poly (alkyl methacrylates) was determined by conducting ultrasonic degradation of PMMA, PEMA and PBMA at 30 °C in toluene. A typical time evolution of the molecular weight distribution observed experimentally is shown in Fig. S1 (see supporting information). The variation of $\ln Y$ with sonication time for the experimental data is shown in Fig. 1 and is linear, as indicated by Eq. (22). The degradation rate coefficient (k_1) is directly obtained by dividing the slope of the regressed line with the limiting molecular weight. The k_1 ($\times 10^8 \text{ mol g}^{-1} \text{ min}^{-1}$) obtained from the linearly regressed line for the degradation of PMMA, PEMA and PBMA in toluene are 4.8, 5.3 and 6.3, respectively. The value of k_1 increases with the increase in number of carbon atoms in alkyl group chain length, i.e., PBMA > PEMA > PMMA. We hypothesize that, similar to the polymer in solid state, the movement of main chain in the polymer in these cases increases with the length of side chain that leads to the molecular chain scission in the main chain of the polymer. A similar trend has been reported for the thermal degradation of poly (alkyl methacrylates) [33].

The effect of different solvents at 30 °C (Fig. 2), the effect of temperature (30–60 °C) (Fig. 3) in chlorobenzene on the ultrasonic degradation of PBMA was investigated. The effect of solvent and temperature can be represented by a change in vapor pressure and viscosity. The vapor pressure and viscosity of the solvents were obtained from a standard handbook [37].

The rate coefficient k_1 decreased with an increase in vapor pressure and is shown in Fig. 4a and b. This is because when vapor pressure increases, more solvent vaporizes inside the microscopic bubbles. This leads to the cushioning effect [1] during their expansion that lowers the intensity of the shock wave resulting in lower degradation [3,16].

The ultrasonic degradation is a fluid mechanical process and thus viscosity of the solvent also plays an important role in determining the degradation rate. The variation of degradation rate coefficient with the viscosity is shown in Fig. S2 (see supporting

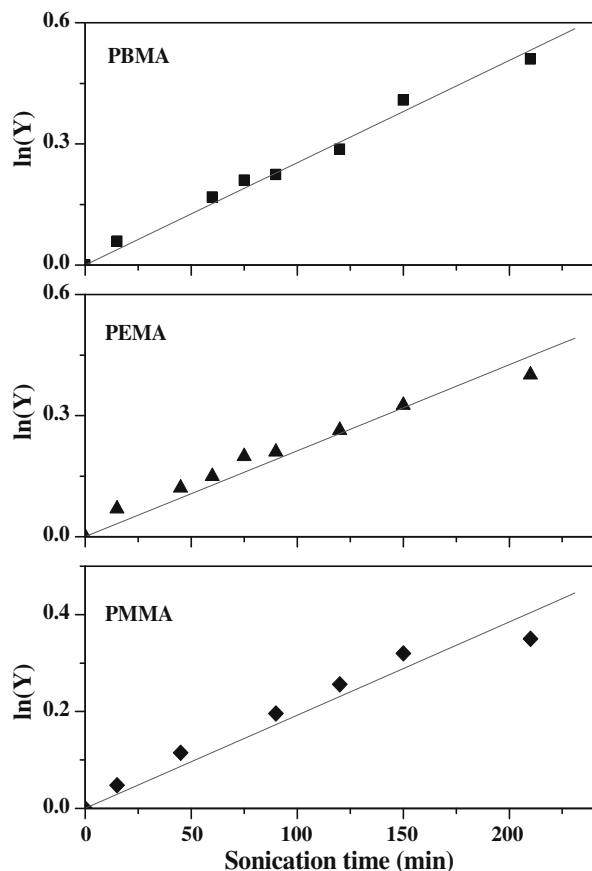


Fig. 1. Variation of $\ln(Y)$ with sonication time in toluene at 30 °C for various poly (alkyl methacrylate)s. The slopes of these linearly regressed lines correspond to the rate coefficient multiplied by the limiting molecular weight.

information). The degradation rate coefficient of PBMA increases with the increase in viscosity of the solvent due to the hydrodynamic force in the neighborhood of cavitation bubbles, which collapses more rapidly in a high viscosity solution [38]. A polymer chain in a more viscous solvent is more easily oriented and can be fragmented at a lower strain rate leading to higher degradation rates of the polymer in a more viscous solution. Further, the transmission of shock wave is more rapid in high viscosity solution [39] leading to higher degradation rate. However, the role of viscosity is secondary to that of vapor pressure. For example, the increase of the degradation rate constant is linear with viscosity (Fig. S2), but the rate constant increases logarithmically with the decrease in vapor pressure (Fig. 4a and b).

The effect of ultrasound intensity (Fig. 5) on the ultrasonic degradation of PBMA was investigated. The degradation rate coefficient of PBMA increases with increase in ultrasound intensity, as reported for other polymers [3,26]. The relationship between the degradation rate coefficient and intensity is linear (Fig. 6) as observed in other studies [40,41]. This is because an increase in intensity leads to larger cavitation bubbles. Above the cavitation threshold, the bubble reaches the maximum radius and is proportional to the square root of intensity [42,43]. The larger cavitation bubbles collapse and produce high shear forces, so the polymer degrades faster [20] at higher intensities.

The ultrasonic degradation of PBMA in presence of the initiators, AIBN, BPO and DCP was studied. The dissociation constants (k_d) of AIBN, BPO and DCP in ultrasound reported in the experimental section are comparable to the thermal dissociation rate constants of initiators [44] at 70 °C. The degradation rate

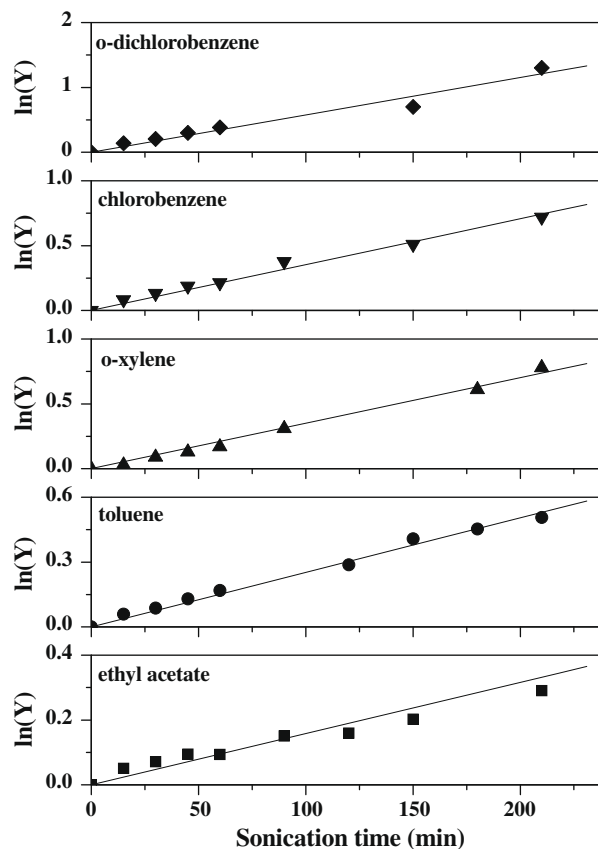


Fig. 2. Variation of $\ln(Y)$ with sonication time for PBMA in various solvents at 30 °C.

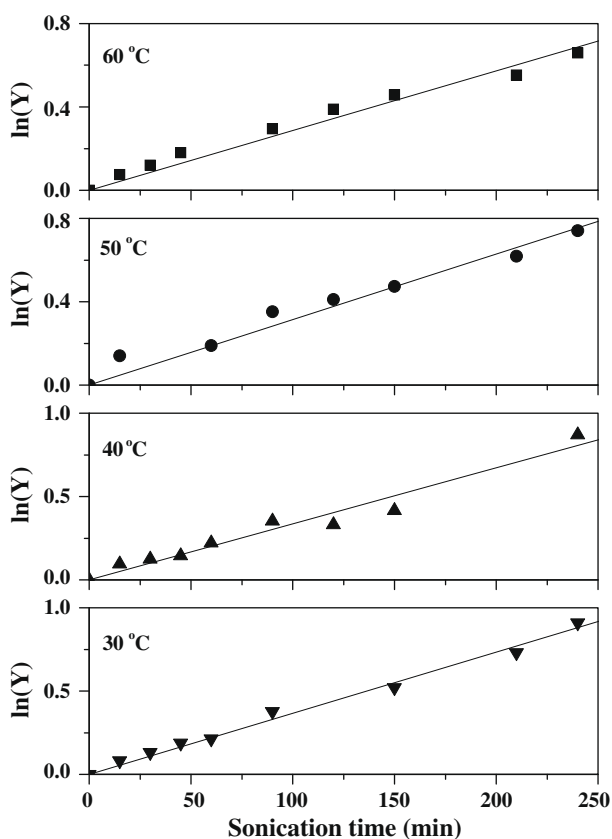


Fig. 3. Variation of $\ln(Y)$ with sonication time for PBMA in chlorobenzene at different temperatures.

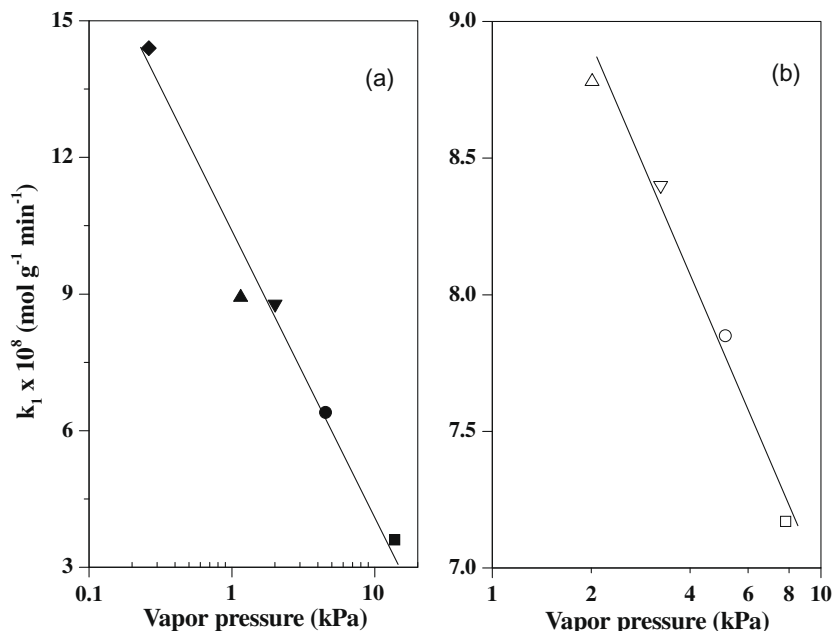


Fig. 4. Variation of degradation rate coefficient of PBMA with vapor pressure of (a) different solvents at 30 °C, ethyl acetate (■), toluene (●), o-xylene (▲), chlorobenzene (▼) and o-dichlorobenzene (◆) (b) chlorobenzene at different temperatures, chlorobenzene at 30 °C (△), 40 °C (▽), 50 °C (○) and 60 °C (□).

coefficient of PBMA in presence of initiator (k_2) was determined by parametric fit of the model (Eq. (22)) with the experimental data obtained from degradation experiments of PBMA at different concentrations of each initiator. Fig. 7 shows the experimental data with the model fit. The model fits the data reasonably well with

the correlation coefficient exceeding 0.95 in all cases. The figure shows the concentration of the initiator in mass units but the calculations are done with the molar concentration of the initiator. The value of k_2 is 130 L/mol in presence of all three initiators, AIBN, BPO and DPO. This indicates that degradation rate of the polymer in presence of initiator depends only on the dissociation constants of initiator. $k_2 = k_D/k_H = 130$ L/mol is consistent with a previous study [10] that observed that $k_D p^{(0)}/k_H = 10^{-3}$ – 10^{-4} because $p^{(0)}$, the molar concentration of the polymer is 10^{-5} . It is, however, prudent to compare the rate of reaction (6) and the reverse of reaction (2). In both reactions, the polymer radical is converted to the stable polymer. In reaction (2), this is due to the hydrogen abstraction, while in reaction (5), it is due to the initiator capping off the polymer radical. If the two reaction rates were equal, then $k_H = k_D D(t)$. In other words, if $k_D D(t)/k_H \gg 1$, then reaction (5) dominates and when $k_D D(t)/k_H \ll 1$, reaction (2) dominates and the initiator will have no effect on the degradation rate of the polymer.

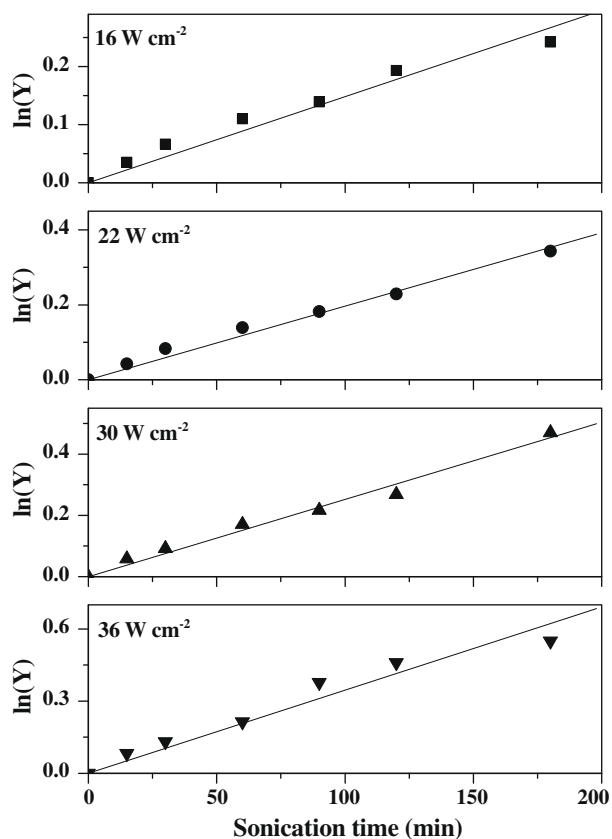


Fig. 5. Variation of $\ln(Y)$ with sonication time for PBMA in chlorobenzene at different ultrasound intensities.

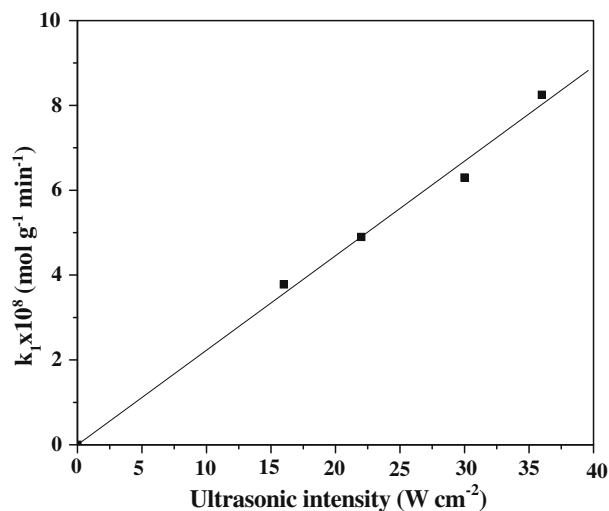


Fig. 6. Variation of degradation rate coefficient of PBMA with ultrasonic intensity.

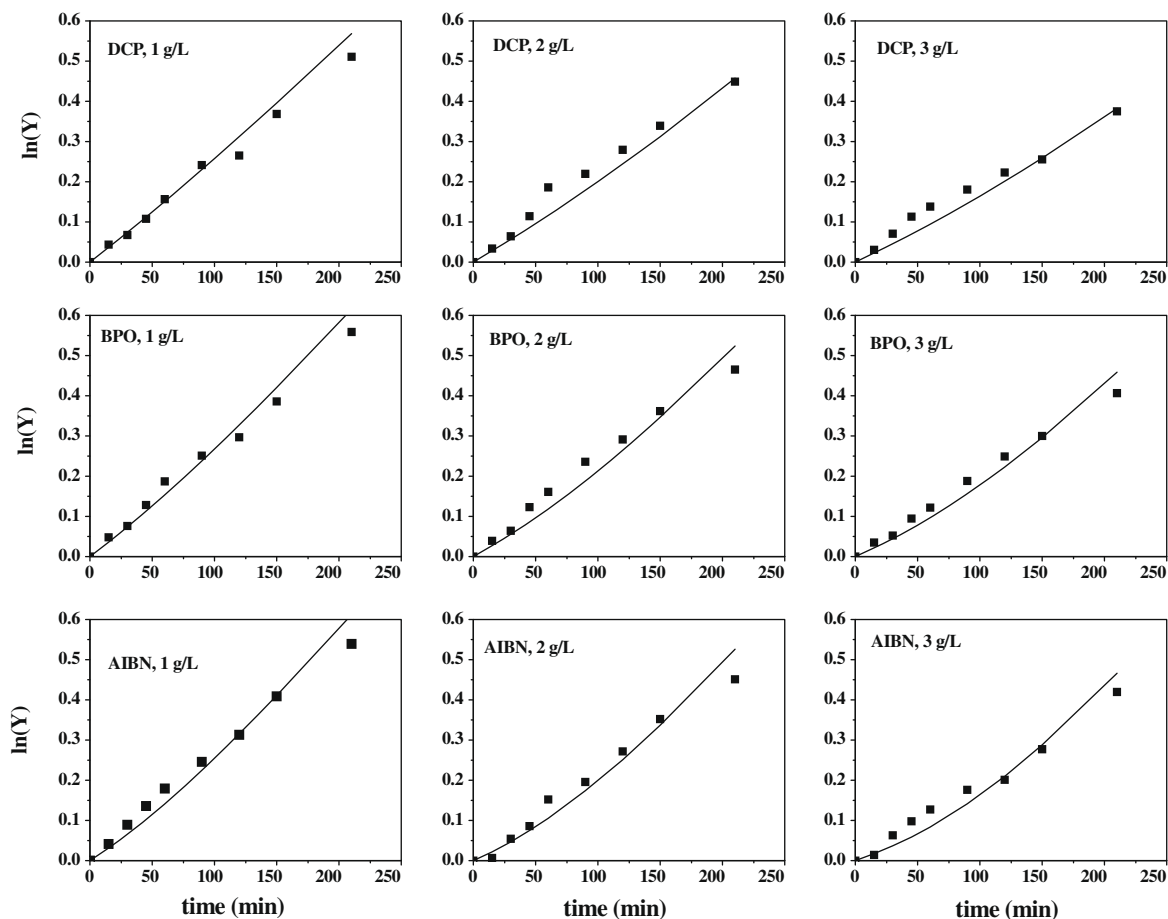


Fig. 7. Variation of $\ln(Y)$ with sonication time of PBMA in chlorobenzene with various initiators. The lines denote the model fit while the points denote the experimental data.

$D(t)$, the molar concentration of the initiator, varies from 10^{-2} mol/L to nearly zero at long time. Because $k_2 = 130$ mol/L in this case, the value of $k_D D(t)/k_H$ varies from nearly unity initially to zero at long time. This long time limit is confirmed by the observation that the limiting molecular weight is the same for the degradation of the polymer irrespective of whether the initiator is present or not. At initial time, $k_D D(t)/k_H$ is nearly unity indicating that the rate of hydrogen abstraction by the initiator (k_D) given by reaction (5) is nearly equal to the rate of hydrogen abstraction (k_H) as given by the reverse reaction in (2). Therefore, the capping of polymer radicals is enhanced by the presence of the initiators, leading to decrease in polymer degradation. Because k_D is independent of the initiator, this implies that the degradation rate of the polymer in presence of any initiator can be directly obtained from the model by inputting the dissociation rate of the initiator.

4. Conclusions

The effect of alkyl group substituents on the ultrasonic degradation of poly (alkyl methacrylate)s was investigated. The degradation rate constant decreases with decrease in number of carbon atoms in the alkyl substituents and follows the order PBMA > PEMA > PMMA. The ultrasonic degradation of PBMA was determined in various solvents, at different temperatures and at different ultrasound intensities. The degradation rate coefficient increases logarithmically with the decrease in vapor pressure and increases with the increase in viscosity of the solvent and ultrasound intensity. Finally the effect of different initiators on the degradation rate of PBMA was determined. These initiators undergo cleavage and

produce free radicals. While one would expect that these free radicals enhance the degradation of the polymer, they cap off the polymer radicals resulting in lower degradation rates of the polymer. A continuous distribution model based on a radical mechanism was developed and used to determine the degradation rate coefficients. The rate coefficient for the interaction of the polymer radical with the initiator is, however, independent of the initiator.

Acknowledgements

The corresponding author thanks the department of Science and Technology, India for Swarnajayanthi fellowship and financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ultsonch.2008.08.007.

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