Ultrasonic degradation of poly(methyl methacrylate-co-alkyl acrylate) copolymers

Vinod Kumar Konaganti, Giridhar Madras *

Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

ABSTRACT

The copolymers, poly(methyl methacrylate-co-methyl acrylate) (PMMAMA), poly(methyl methacrylate-co-ethyl acrylate) (PMMAEA) and poly(methyl methacrylate-co-butyl acrylate) (PMMABA), of different compositions were synthesized and characterized. The effect of alkyl acrylate content, alkyl group substituents and solvents on the ultrasonic degradation of these copolymers was studied. A model based on continuous distribution kinetics was used to study the kinetics of degradation. The rate coefficients were obtained by fitting the experimental data with the model. The linear dependence of the rate coefficients on the logarithm of the vapor pressure of the solvent indicated that vapor pressure is the crucial parameter that controls the degradation process. The rate of degradation increases with an increase in the alkyl acrylate content. At any particular copolymer composition, the rate of degradation follows the order: PMMAMA > PMMAEA > PMMABA. It was observed that the degradation rate coefficient varies linearly with the mole percentage of the alkyl acrylate in the copolymer.

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1. Introduction

Ultrasound has been used in several applications such as polymer degradation [1], copolymerization [2], emulsion polymerization [3], organic reactions [4], and for removing high molecular weight tails from fractionated polymers. Polymer degradation by ultrasound has been used as an effective technique for the degradation of polymer compounds because of its *nonrandom* nature of depolymerization unlike thermal and chemical degradation methods [1]. The effect of ultrasound is due to cavitation of microbubbles and collapsing walls of the microbubbles, which produce intense shear on polymer molecules near the bubbles [1]. Since the polymer scission occurs by mechanical shearing, the scission occurs primarily at the mid point of the chain [5].

The effect of different parameters such as ultrasound intensity, temperature, solvent, dissolved gases, polymer concentration, initial molecular weight, viscosity, surface tension and alkyl group substituents on the ultrasonic degradation of different polymers has been reported in literature [6–9]. The kinetic studies for the ultrasonic degradation of polymer solutions by using continuous distribution kinetics [5,8,9] and viscometry [7,10,11] have been reported. Akyüz et al. [12,13] have compared several theoretical and phenomenological models for the evolution of molecular weight with sonication time and observed that the

models that use continuous distribution kinetics describe the results adequately [12,13]. Taghizadeh and Mehrdad have determined the kinetics for the ultrasonic degradation of poly(vinyl alcohol) and poly(vinyl acetate) using viscometry [14,15]. A few studies on the ultrasonic treatment/degradation of polymer blends and melts have also been reported in literature [16–18].

Alkyl methacrylates can form copolymers with alkyl acrylates [19] and these poly(methyl methacrylate-co-alkyl acrylate) copolymers are used in adhesives, coatings and in multigrade lubricating oils [20]. One of the important applications of ultrasound is to investigate the stability of polymer additives. So, it is very useful to study the ct of ultrasound on the stability of these copolymers.

To the best of our knowledge, this is the first detailed kinetic study on the ultrasonic degradation of poly(methyl methacrylate-co-alkyl acrylate) copolymers in solution. In the present study, different compositions of poly(methyl methacrylate-co-methyl acrylate) (PMMAMA), poly(methyl methacrylate-co-ethyl acrylate) (PMMAEA) and poly(methyl methacrylate-co-butyl acrylate) (PMMABA) copolymers were synthesized and ultrasonic degradation of these polymers was studied. The objective of this study was to investigate the effect of composition (percentage of monomer), alkyl group substituents and solvents on the ultrasonic degradation of poly(methyl methacrylate-co-alkyl acrylate) copolymers. Continuous distribution kinetics was used to model the kinetics of degradation process and the degradation rate coefficients were obtained by fitting the experimental data with the model. It is shown for the first time that the degradation rate coefficient varies linearly with the mole percentage of the alkyl acrylate in the copolymer.

* Corresponding author. Tel.: +91 80 22932321; fax: +91 80 23600683.
  E-mail addresses: giridhar@chemeng.iisc.ernet.in, giridharmadras@gmail.com
(G. Madras).

2. Experimental details

2.1. Materials

Methyl methacrylate (MMA), methyl acrylate (MA), ethyl acrylate (EA) and n-butyl acrylate (BA) were purchased from Sigma Aldrich (USA) and washed with 5% caustic solution to remove the inhibitor followed by distillation under pressure. The solvents tetrahydrofuran, o-dichlorobenzene, chlorobenzene, toluene, o-xylene and benzene were purchased from S.D. Fine chemicals (India). The solvents were distilled and filtered using 0.2 μm nylon filter paper before use. The initiator, azo-bis-isobutyronitrile (AIBN) was purchased from S.D. Fine chemicals (India). Polystyrene standards, used for the calibration of molecular weights, were procured from Polymer labs (USA).

2.2. Polymerization

All the homopolymers PMMA, PMA, PEA, PBA and different compositions of PMMAMA, PMMAEA, and PMMABA copolymers were synthesized by solution polymerization technique using AIBN as the initiator at 60 °C. Calculated amounts of monomers (MMA, MA, EA and BA), benzene and AIBN were taken in culture tubes and the mixture was flushed with inert gas N_2 for 15 min. The tubes were then kept in the incubator shaker maintained at 60 °C. The homopolymers and copolymers formed were precipitated in methanol and dried at 50 °C. The initial molecular weight, limiting molecular weight and polydispersity for all the homopolymers and the copolymers are shown in Table S1 (see Supplementary information).

2.3. NMR characterization

^{1}H NMR (400 MHz, Bruker) spectroscopy was used to determine the composition of the synthesized copolymers, using $CDCl_3$ as solvent and tetramethylsilane as a reference substance for resonance frequency.

2.4. Degradation experiments

Polymer solutions of concentration 2 g L^{-1} for all the homopolymers and copolymers of different compositions in o-dichlorobenzene were prepared to study the effect of alkyl acrylate content. PMMAMA-36 (36 mol percentage of methyl acrylate) polymer solutions of concentration 2 g L^{-1} in different solvents (o-dichlorobenzene, chlorobenzene, toluene, o-xylene and benzene) were prepared to study the effect of solvent. 70 mL of polymer solution was ultrasonically degraded by using a horn-type ultrasonic processor (Vibronics, India) with an intensity of 36 W cm^{-2} and frequency of 25 kHz at 30 °C. The temperature of the solution was maintained constant (±1 °C) using a thermostated water bath. The samples were collected at various intervals of time for further analysis by gel permeation chromatography (GPC). The limiting molecular weight was obtained by conducting each experiment for eight hours and it is listed in Table S1 (see Supplementary information).

2.5. Gel permeation chromatography (GPC) analysis

The molecular weight distributions (MWDs) of the samples were determined by using GPC. The GPC consists of a high pressure liquid chromatography (HPLC) pump (Waters 501), three size exclusion columns (Styragel HR 5E, HR 4 and HR1) in series packed with poly(styrene-divinyl benzene), a differential refractometer (Waters RI 2410) to monitor the refractive index and a data acqui-

sition system to store the data. The sonicated samples were injected through a Rheodyne 7725i valve with a sample loop of 50 μL. The eluent tetrahydrofuran (THF) was pumped at a flow rate of 1 mL min^{-1}. The system was calibrated by using narrow molecular weight polystyrene standards. The same universal calibration curve was used for all the polymers and copolymers. Multiple analyses to determine the molecular weight of the same sample indicated the error was less than 2% while the rate coefficients determined in the study have errors less than 4%.

3. Theoretical model

The mid chain scission of polymer chain under ultrasound irradiation yields two daughter products nearly having same chain length. Thus, the overall degradation reaction with a rate coefficient, κ, can be represented by

$$P(x) \rightarrow 2P(x/2) \tag{1}$$

where $P(x)$ represents polymer chain of molecular weight x, whose molar concentration can be indicated by $p(x,t)$. By applying continuous distribution kinetics to the above equation it becomes [5,21]

$$\frac{\partial p(x,t)}{\partial t} = -\kappa(x)p(x,t) + 2\int_x^\infty \kappa(x')p(x',t)\delta\left(x - \frac{x'}{2}\right)dx' \tag{2}$$

The degradation coefficient, $\kappa(x)$, is assumed to be of the form $\kappa(x) = k(x - x_l)$, where x_l is the limiting molecular weight [21]. This clearly indicates that no further degradation takes place at limiting molecular weight i.e. when $x = x_l$ which is consistent with the experimental observation. Further, the rate coefficient, k, is independent of molecular weight and thus the rate coefficient for different systems can be compared even if the initial molecular weights of the polymers are different. The moments of the MWDs are defined as

$$p^{(j)}(t) = \int_0^\infty p(x,t)x^j dx \tag{3}$$

Applying the above moment operation to Eq. (2), yields [21]

$$\frac{dp^{(j)}}{dt} = k(2^{1-j} - 1)(p^{(j+1)} - p^{(j)}x_l) \tag{4}$$

The above equation represents the variation of MWD moments of the polymer with time, and is solved by using corresponding initial conditions. The above equation is solved for the zeroth moment ($j = 0$) with the initial condition, $p^{(0)}(t = 0) = p_0^{(1)}$ to get

$$\left(\frac{p^{(1)} - p_0^{(0)}x_l}{p^{(1)} - p^{(0)}x_l}\right) = e^{kx_l t} \tag{5}$$

where $p^{(0)}$ and $p^{(1)}$ are zeroth and first moments which represent the molar and mass concentrations of the polymer. The variation of the first moment obtained by putting $j = 1$ in Eq. (4) indicates that the variation with time is zero. Thus, mass is conserved and $p^{(1)} = p_0^{(1)}$ at all times. The number average molecular weight, M_n, is defined as $p^{(1)}/p^{(0)}$. So, the Eq. (5) can be rewritten as [21]

$$\ln\left(\frac{\frac{1}{M_{n0}} - \frac{1}{x_l}}{\frac{1}{M_n} - \frac{1}{x_l}}\right) = \ln H = kx_l t \tag{6}$$

where $H = [(1/M_{n0}) - (1/x_l)]/[(1/M_n) - (1/x_l)]$. The above equation represents the variation of M_n with time t, in terms of initial molecular weight, M_{n0}, and limiting molecular weight, x_l. The values of the degradation rate coefficient at various conditions are obtained by fitting the experimental data with the model.

4. Results and discussion

4.1. NMR characterization of copolymers

^{1}H NMR spectroscopy was used to determine the composition of the copolymers. In case of PMMAEA and PMMABA copolymers, the MMA shows a singlet peak around δ = 3.8 corresponding to methoxy group (–OCH$_3$) of the ester linkage. EA shows a quartet and BA shows a triplet corresponding to methyleneoxy group (–OCH$_2$) of the ester linkage around δ = 4.2 [22–24]. The monomer composition in the copolymers can be determined from the integrated peak areas by using the following equation [25,26].

$$y_m = \frac{\frac{2a_m}{3a_e}}{1 + \frac{2a_m}{3a_e}} \tag{7}$$

where y_m is the mole fraction of MMA in the copolymer, a_m is the methoxy peak area corresponding to MMA and a_e is the methyleneoxy peak area corresponding to EA/BA, the factor 2/3 arises from the number of corresponding protons.

For PMMAMA copolymers, the following procedure was used. Because both the monomers MMA and MA have the same characteristic group i.e., the methoxy (–OCH$_3$) group of the ester linkage, the total proton difference between MMA (8 protons) and MA (6 protons) was used to determine the composition of the copolymer. If X is the molar ratio of MMA/MA in the copolymer, then

$$\frac{I_{total}}{I-OCH_3} = R = \frac{(8X+6)}{(X+1)3} \tag{8}$$

$$X = \frac{(3R-6)}{(8-3R)} \tag{9}$$

where I_{total} and I–O–CH$_3$ are the integrals of peaks corresponding to all the protons and –OCH$_3$ peaks, respectively. If y_m is the mole fraction of MMA in the copolymer, then [26]

$$\frac{I_{total}}{I-OCH_3} = R = \frac{(8y_m + 6(1-y_m))}{(3y_m + 3(1-y_m))} = \frac{6+2y_m}{3}; y_m = \frac{(3R-6)}{2} \tag{10}$$

Fineman-Ross method [27] was used to determine the reactivity ratios of the monomers using NMR composition data. The copolymer equation is

$$\frac{d[M_1]}{d[M_2]} = \left(\frac{M_1}{M_2}\right)\left(\frac{r_1 M_1 + M_2}{r_2 M_2 + M_1}\right) \tag{11}$$

where $d[M_1]$ and $d[M_2]$ represent the compositions of monomers in the copolymer while M_1 and M_2 represent the concentrations of monomers in the feed and r_1 and r_2 are the monomer reactivity ratios of MMA and MA/EA/BA, respectively. This equation can be linearized to

$$G = r_1 F - r_2 \tag{12}$$

where $G = \left(\frac{y(z-1)}{z}\right)$, $F = \left(\frac{y^2}{z}\right)$, $y = \left(\frac{M_1}{M_2}\right)$ and $z = \left(\frac{d[M_1]}{d[M_2]}\right)$ where y and z are ratios of monomers in the feed and in the copolymer, respectively.

The Fineman-Ross plot for the copolymers PMMAMA, PMMAEA and PMMABA are shown in Fig S1 (see Supplementary information). The monomer reactivity ratios for the copolymer PMMAMA are r_1 (MMA) = 1.55 and r_2 (MA) = 0.26, for the copolymer PMMAEA are r_1 (MMA) = 2.04 and r_2 (MA) = 0.23 and for the copolymer PMMABA are r_1 (MMA) = 2.98 and r_2 (BA) = 0.31 and the values are comparable with the values reported in literature [24–26]. The product of reactivity ratios for each copolymer is less than unity indicating that all the copolymers are random copolymers.

4.2. Ultrasonic degradation

4.2.1. Effect of alkyl acrylate content

The effect of alkyl acrylate on the ultrasonic degradation of PMMAMA, PMMAEA, and PMMABA copolymers was investigated by conducting the experiments over the entire range of composition for all the copolymers at 30 °C using o-dichlorobenzene as solvent. The variation of ln(H) with sonication time for different compositions of PMMAMA copolymer is shown in Fig. 1. From Fig. 1, it is clear that the experimental data fits well to the model (Eq. (6)). The degradation rate coefficient is obtained by dividing the slope with limiting molecular weight. Similar plots were observed for different compositions of PMMAEA and PMMABA copolymers, as shown in Figs. 2 and 3, respectively. The values of degradation coefficient for the ultrasonic degradation of all the homopolymers and copolymers (of different compositions) are listed in Table S2 (see Supplementary information).

The degradation rate coefficient, k, increases linearly with increase in alkyl acrylate composition (mole percentage of the alkyl acrylate) in the copolymer, as shown in Fig. 4, indicating that the rate of ultrasonic degradation increases with the increase in alkyl acrylate content of the copolymer. This can be attributed to the effect of copolymer composition on the mechanical properties of the polymers. The MMA units can be considered as hard sequences where as the alkyl acrylate units can be considered as soft sequences [28,29]. With increasing alkyl acrylate content in the copolymer, it behaves as an elastomeric material [29] and thus the polymer chains readily undergo deformation and rupture nearly at the mid point of the polymer chain under ultrasonic irradiation.

The order of degradation for the homopolymers follows the order: PMMA < PBA < PEA < PMA, as evident from the values of the rate coefficients, as shown in Table S2 (see Supplementary information). The order of the rate of degradation, PBA < PEA < PMA, shows that the rate of ultrasonic degradation decreases with the
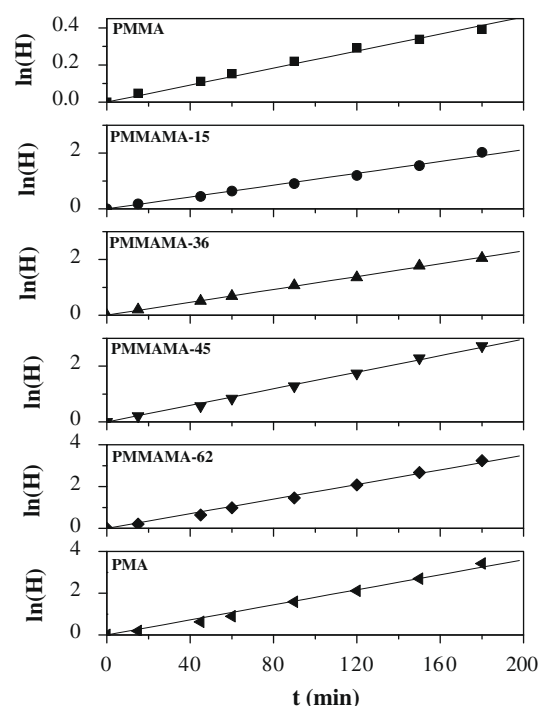

Fig. 1. Variation of ln(H) with sonication time in o-dichlorobenzene at 30 °C for different compositions of PMMAMA copolymers. Legend: (■) 0 mol% MA(PMMA), (●) 15 mol% MA, (▲) 36 mol% MA, (▼) 45 mol% MA, (♦) 62 mol% MA and (◄) 100 mol% MA (PMA). The solid lines are model fit.
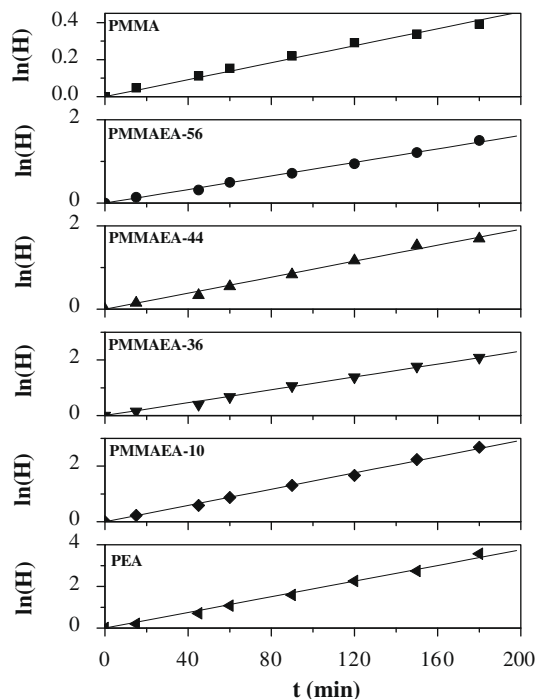
Fig. 2. Variation of ln(H) with sonication time in o-dichlorobenzene at 30 °C for different compositions of PMMAEA copolymers. Legend: (■) 0 mol% EA(PMMA), (●) 10 mol% EA, (▲) 36 mol% EA, (▼) 44 mol% EA, (♦) 56 mol% EA and (◄) 100 mol% EA (PEA). The solid lines are model fit.
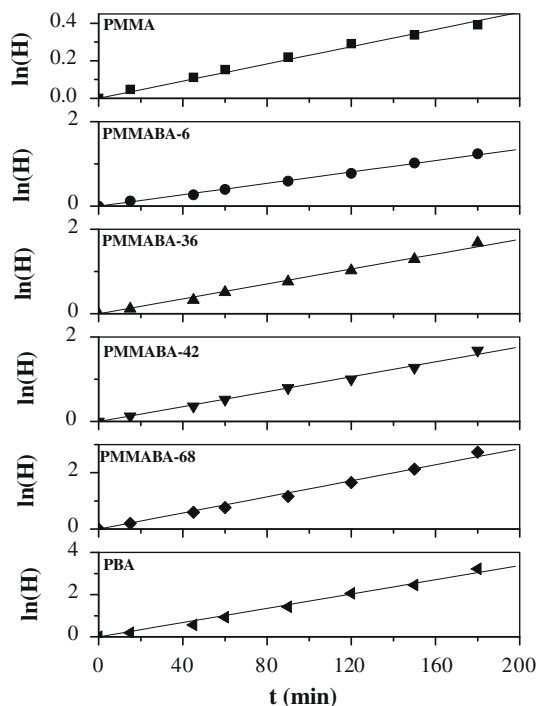

Fig. 3. Variation of ln(H) with sonication time in o-dichlorobenzene at 30 °C for different compositions of PMMABA copolymers. Legend: (■) 0 mol% BA(PMMA), (●) 6 mol% BA, (▲) 36 mol% BA, (▼) 42 mol% BA, (♦) 68 mol% BA and (◄) 100 mol% BA (PBA). The solid lines are model fit.

length of the side chain. This result is in contrast to that observed [30] for the ultrasonic degradation of poly (alkyl methacrylates) where the rate of ultrasonic degradation increased with chain length of the side chains and followed the order, PBMA > PEMA >
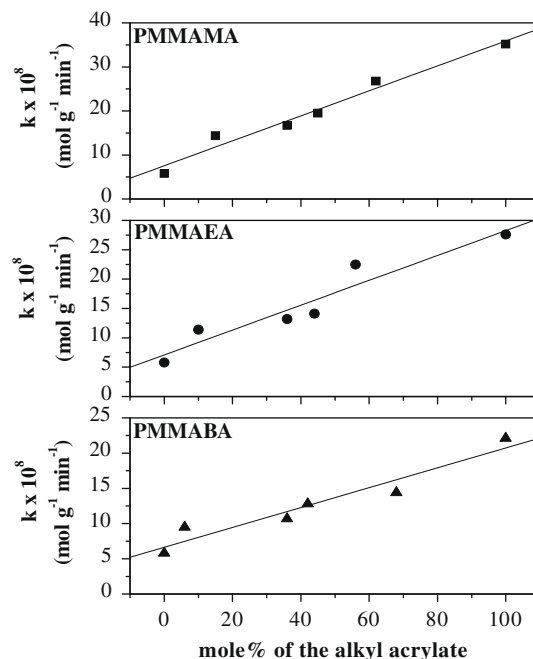

Fig. 4. Variation of degradation rate coefficient with mole percentage of the alkyl acrylate (MA/EA/BA). Legend: (■) PMMAMA, (●) PMMABA and (▲) PMMAEA.

PMMA. PBA refers to poly (butyl acrylate) while PBMA refers to poly (butyl methacrylate). This is because the order of ultrasonic degradation follows the order of thermal degradation. In case of thermal degradation [31] of poly (alkyl methacrylates), the order is PBMA > PEMA > PMMA. Similarly, for the thermal degradation [32] of poly(alkyl methacrylates), the rate follows the order PBA < PEA < PMA. Therefore, the results indicate the variation of the rate coefficient of ultrasonic degradation is similar to the thermal stability of the polymer.

4.2.2. Effect of alkyl group substituents

Based on the values of the degradation rate coefficient (Table S2, Fig. 4), at any particular alkyl acrylate composition (mole percentage), the rate of ultrasonic degradation follows the order: PMMAMA > PMMAEA > PMMABA. This indicates that the rate of degradation decreases with increase in alkyl group (alkyl acrylate) chain length, which can be attributed to the delocalization of electrons [33]. At any particular mole percentage of alkyl acrylate, the rate of degradation increases with the decrease in size of the alkyl group substituent. Similar results were observed for the ultrasonic degradation of poly(n-alkyl acrylates) [9].

4.2.3. Effect of solvents

The effect of solvents on the ultrasonic degradation of poly (methyl methacrylate-co-alkyl acrylate) copolymers was investigated by conducting experiments on a typical copolymer, PMM-AMA-36 (36 mol percentage of MA) at 30 °C using different solvents. The variation of ln(H) with sonication time for the ultrasonic degradation of PMMAMA-36 for different solvents is shown in Fig. 5. The effect of solvent on the degradation rates can be mainly attributed to vapor pressure and viscosity [8,34]. The variation of degradation rate coefficient, k, with vapor pressure and viscosity are shown in Fig. 6a and b, respectively. The values of vapor pressure and viscosity of the solvents were taken from a standard handbook [35].

The degradation rate coefficient, k, increases with a decrease in vapor pressure as shown in Fig. 6a. As the vapor pressure of the solvent increases, the amount of vapor that enters the bubbles
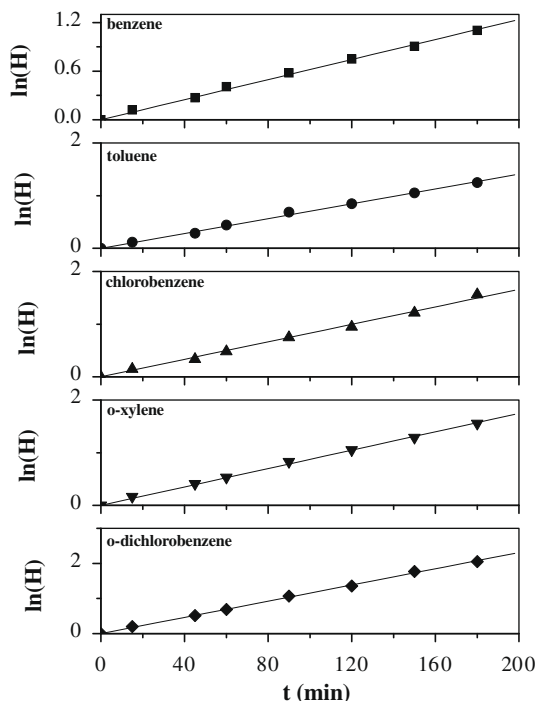
Fig. 5. Variation of ln(*H*) with sonication time for PMMAMA-36 (36 mol% of MA) at 30 °C in different solvents. Legend: (■) benzene, (●) toluene, (▲) chlorobenzene, (▼) *o*-xylene, and (♦) *o*-dichlorobenzene. The solid lines are model fit.
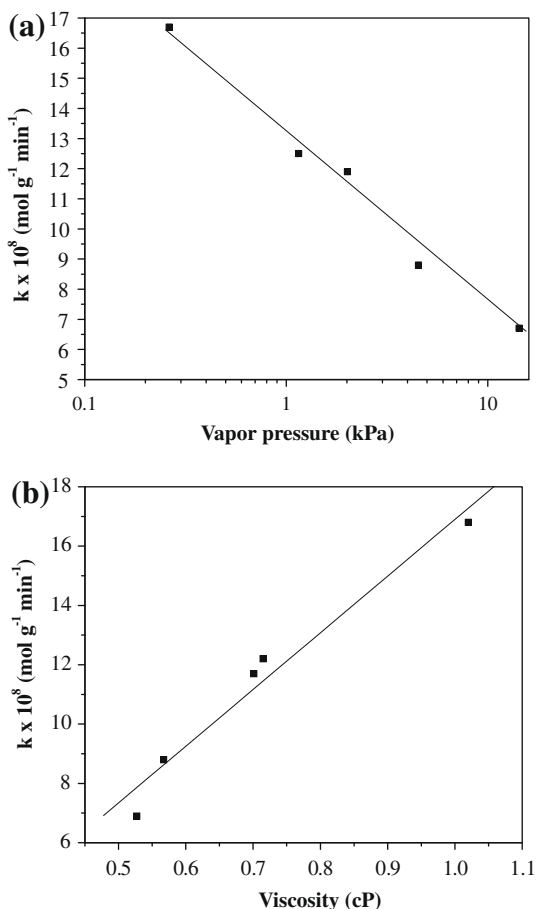

Fig. 6. (a) Variation of degradation rate coefficient, *k*, with (a) vapor pressure of the solvent and (b) viscosity of the solvent.

increases, which is responsible for the cushioning effect [1,6,8,9,36]. The cushioning effect reduces the effect of shock waves and thus the rate of degradation. Thus, the rate of polymer degradation is higher in the presence of solvents with lower pressures. The degradation rate coefficient, *k*, increases linearly with increase in viscosity of the solvent as shown in Fig. 6b. This may be because of the rapid transmission of shock waves in high viscosity solutions and oriented polymer chains that favor the fragmentation of polymer chains at low strain rates in high viscosity solutions [37] compared to low viscosity solutions. The effect of vapor pressure on the ultrasonic degradation is very high compared to viscosity, which is clear from the exponential variation of degradation rate coefficient, *k*, with vapor pressure as shown in Fig. 6a The effect of solvent on the ultrasonic degradation of the copolymers observed in this study is consistent with the results reported in literature for the degradation of polymers such as poly(ethylene oxide), poly(*n*-alkyl acrylates), poly(vinyl acetate) and poly(vinyl chloride) [8,9,21,34].

5. Conclusions

The ultrasonic degradation of three different types of poly(methyl methacrylate-co-alkyl acrylate) (PMMAMA, PMMAEA and PMMABA) copolymers over the entire range of composition was investigated. Continuous distribution kinetics was used to model the kinetics of the degradation and the rate coefficients were obtained by fitting the experimental data with the model. The values of degradation coefficient indicated that the rate of degradation increases with increase in mole percentage of alkyl acrylate in the copolymer. The rate of degradation of these copolymers, at any particular copolymer composition follows the order: PMMAMA > PMMAEA > PMMABA. The effect of different solvents on the ultrasonic degradation of PMMAMA-36 was studied. The degradation rate coefficient increased with a decrease in the logarithm of vapor pressure and increased linearly with increase in viscosity, indicating that vapor pressure is the main factor for controlling the degradation process.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ultsonch.2009.08.016.

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