Continuous Distribution Kinetics for Microwave-Assisted Oxidative Degradation of Poly(alkyl methacrylates)

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The microwave-assisted oxidative degradation of poly(alkyl methacrylates) namely poly(methyl methacrylate), poly(ethyl methacrylate) (PEMA), and poly(butyl methacrylate) was investigated. The kinetic parameters were compared to that obtained by thermal oxidative degradation. The molecular weight distributions (MWDs) were simulated using continuous distribution kinetic models. The MWD of polymer was expressed as a γ-distribution, and the mathematical solutions were developed in terms of γ-distribution parameters. The MWD of degradation mixture approaches an exponential distribution under both oxidative thermal degradation and microwave-assisted oxidative degradation of poly(alkyl methacrylates), indicating random chain scission. The degradation of PEMA was investigated in the presence of three different oxidizers. The hydrogen abstraction from polymer and the oxidative random chain scission of polymer radicals were found to be the important steps in the overall mechanism of microwave-assisted oxidative degradation of poly(alkyl methacrylates). The model developed can be used to predict degradation rate of the polymer in the presence of any oxidizers by knowing only the dissociation rate constant of the oxidizer. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 2164–2173, 2008

Keywords: microwaves, γ-distribution, poly(alkyl methacrylates), oxidative-degradation

Introduction

The enhancement of polymer degradation by peroxide addition when compared with thermal degradation in solution has been extensively studied.[1–5] The degradation in the presence of peroxide occurs at lower temperature, resulting in significant energy savings. The oxidative thermal degradation of polymers in solution, that is, in the presence of oxidizer occurs only by random chain scission.[1–5] The overall mechanism in degradation of polymer films involves both chain scission and cross-linking reactions.[6,7] The cross-linking reactions make the system more complex, and there are difficulties involved in obtaining quantitative kinetic information from such solid samples.[8] The crosslinking probabilities can be reduced by using the liquid phase.[8] A detailed review[9] on kinetics and mechanism of oxidative degradation has been published. The use of microwave energy for chemical reactions has become increasingly popular.[10,11] Excellent efficiency has been observed for the microwave assisted reactions, and it has many advantages like even distribution of heat and better control over the heating process.[12] A detailed review on microwave-assisted chemical synthesis has been published.[11] Microwave-assisted polymerizations are proven to be more efficient than thermal techniques, for monomers containing polar groups that favor the absorption of microwaves. The emulsion polymerization under microwave radiation has been studied, and significant savings of energy and time compared to conventional methods has been reported.[13]

The rate of polymer degradation under microwave radiation increased for degradation in solid phase (high-density

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polyethylene and aluminum polymer laminates)[12] and in solution (oxidative degradation of polystyrene).[14] The dynamics of molecular weight distributions (MWDs) have been investigated extensively for the polymer degradation in the absence of oxidizer.[15–18] There are very few studies, in which MWDs have been evaluated for the oxidative degradation of polymers.[3] Madras and McCoy[3] investigated the oxidative degradation of polystyrene in solution and developed a continuous-distribution model for evaluating MWDs. The γ-distribution is a general representation of molecular weight distributions.[15–18] Distributions such as Gaussian, Poisson, exponential, rectangular, and delta distributions are special cases of γ-distribution. The time evolution of MWDs was determined as variations of γ-distribution parameters with time.[15–18] The major difference in obtaining mathematical solution between microwave-assisted oxidative degradation and oxidative degradation under conventional heating is the variation of rate coefficients with experimental time under microwave radiation. This is because the temperature in the microwave oven is a function of time.

Poly(alkyl methacrylates) are widely used in various applications. It is important to investigate the effect of alkyl group substituents in these series of polymers to find the best polymer for a particular application. The effect of alkyl group substituents for the thermal degradation of poly(alkyl methacrylates) has been investigated in both subcritical and supercritical fluids.[19]

The objectives of this work are to (a) determine the enhancement in degradation rate of microwave-assisted oxidative degradation when compared with that of thermal oxidative-degradation, (b) predict the overall polymer degradation rate in the presence of different oxidizing agents, (c) develop kinetic models to predict the complete MWDs for the microwave-assisted oxidative degradation of polymers in solution, and (d) determine the effect of different alkyl group substituents on the degradation rate.

Experimental

Materials

Methyl methacrylate, poly(ethyl methacrylate) (PEMA) (number–average molecular weight, M_{n0} = 95,800 and polydispersity, PD = 1.25), and poly(butyl methacrylate) (PBMA) (M_{n0} = 90,000 and PD = 1.20) were obtained from Sigma Aldrich. Poly(methyl methacrylate) (PMMA) (M_{n0} = 340,000 and PD = 1.20) was synthesized by bulk polymerization technique with benzoyl peroxide (BPO) as the initiator. The monomer was purified by washing with 5% caustic solution followed by washing with distilled water and distilled before use. The initiators, BPO and dicumyl peroxide (DCP), and solvents, tetrahydrofuran (THF) and chlorobenzene, were procured from S.D. Fine Chemicals (India), and solvents were filtered through 0.2-μm nylon filter paper. The initiator azobis isobutyro nitrile (AIBN) was obtained from Kemphasol (India) and purified by precipitating in acetone and recrystallized.

Degradation experiments

PEMA of concentration 2 g/L in dichlorobenzene was used for thermal oxidative degradation. The initial concentration of BPO was kept constant at 10 g/L. About 15 mL of the polymer solution was taken in culture tubes with screw caps. The experiments were conducted in the temperature range of 60–80°C. The temperature was maintained by a water bath controlled by a PID controller. The experiments were also carried out without initiators under the same experimental conditions, and it was observed that no degradation of the polymer occurred in the absence of initiator.

For microwave-assisted degradation studies, a domestic microwave oven with a magnetron source was used (Essentia, India, 700 W, 2.45 GHz). The degradation of poly(alkyl methacrylates) of 50 mL volume with 2 g/L concentration was conducted in 100-mL glass beaker. The sample was placed at the center of the oven, and it was rotated to maintain uniform temperature in the reaction mixture. The degradation of PEMA in the presence of three different oxidizers, BPO, DCP, and AIBN, under the same experimental conditions was studied to investigate the effect of oxidizers. The oxidizer concentration of 10 g/L was used for the degradation studies in the presence of BPO and DCP, and 5 g/L was used for the degradation studies in presence of AIBN because of its lower solubility limit. The concentration of BPO was varied from 2 to 20 g/L to investigate the oxidizer concentration effect on the degradation. The experiments were conducted in a cyclic operation, and each sample was irradiated for 10 cycles. The cycle time for each cyclic operation is τ s that consists of different heating time (t_h) and constant cooling time (t_c = 60 s). A sample of 0.5 mL volume was collected after 1, 2, 3, 4, 6, 8, and 10th cycle and analyzed in gel permeation chromatography (GPC). The temperature profile of the reaction mixture in the microwave oven mainly depends on the solvent properties and varies as shown in Figure 1a. The heating cycle time (t_h) was varied from 60 to 100 s, and the irradiated sample was cooled to 25°C by immersing in an ice water bath for a constant set time (t_c) of 60 s to obtain a linear cooling profile by adjusting the stirring of the reaction mixture. The linear heating and cooling period constitutes the triangular temperature profile for each cycle as shown in Figure 1b. Several experiments were conducted in triplicate, and the variation in the rate coefficients was less than 2%.

Sample analysis

The molecular weight distribution of the polymer samples was determined by (GPC) (Waters, USA). The GPC system consists of an isocratic pump, a sample loop (50 μL), three size exclusion columns of varying pore size (HR 5E, HR 3, and HR 0.5; 300 mm × 7.5 mm), and differential refractive index detector. THF with constant flow rate of 1 mL/min was used as eluent through the system, and the columns were maintained at 50°C. The refractive index was continuously monitored and stored digitally using data acquisition system. The chromatograph was converted to molecular weight distribution using a universal calibration curve determined using polystyrene standards (Polymer Lab, UK).

Theoretical Model

Continuous distribution kinetic is the effective tool to determine the dynamics of polymer degradation.[15–18] The

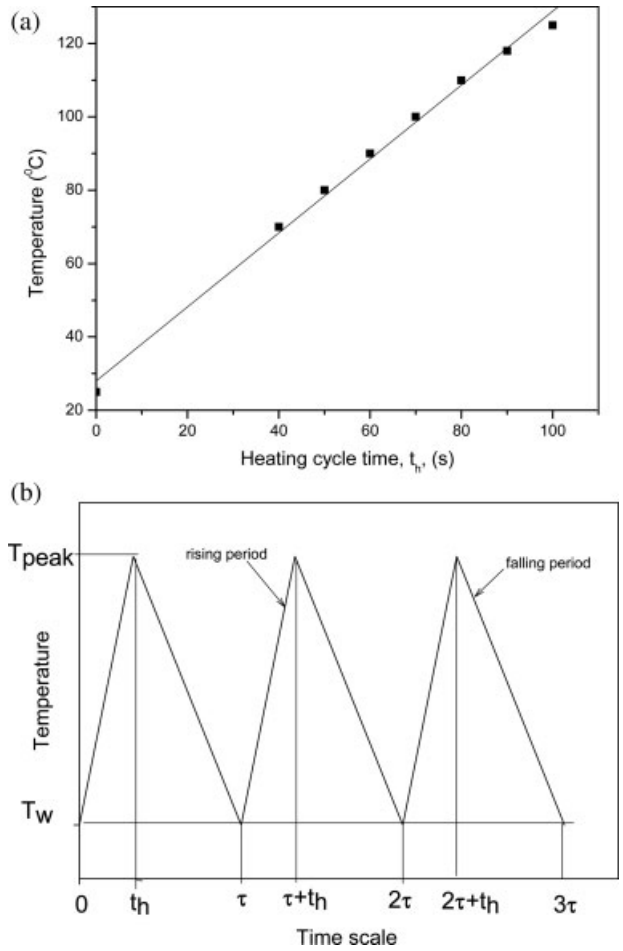

Figure 1. (a) Variation of temperature with heating time; (b) temperature profile for the complete cycle.

polymer, P(x), is considered to be a mixture of number of molecules with molecular weight x as a continuous variable. The MWDs of polymer degradation mixtures during the reaction can be represented by general γ-distribution[15–18] as,

$$p(x,t) = \frac{p^{(1)}(t)(x/\beta)^{(\alpha-1)}\exp(-x/\beta)}{\Gamma(\alpha+1)\beta^2} \tag{1}$$

The MWD as represented by γ-distribution in Eq. 1 has three time-dependent parameters, $p^{(1)}$ representing the first moment of MWD (mass concentration), α and β. For homologous polymers, the number–average and weight-average molecular weights are given as,

$$M_n = p^{(1)}/p^{(0)} \quad \text{and} \quad M_w = p^{(2)}/p^{(1)} \tag{2}$$

For Eq. 1, the number–average and weight-average molecular weight can be written[20] as,

$$M_n = \alpha\beta \quad \text{and} \quad M_w = (\alpha+1)\beta \tag{3}$$

From these expressions, it is clear that first three moments (j = 0, 1, 2) of the MWD fully determine the γ-distribution. The generalized γ-distribution solution (1) requires the evolution of these three parameters with reaction time. These parameters can be determined from first three moments of the MWD. The MWD of the initial polymer-PEMA, measured from GPC, was fitted with γ-distribution (1), and the values of initial parameters are $p^{(1)}$ = 2 g/L, α = 4, and β = 23,950.

For the degradation in the presence of oxidizer, the oxidizer initiates the reaction by the homolytic cleavage followed by the random hydrogen abstraction from the polymer molecule to produce polymer radicals. MWD results showed no evidence of specific products from chain-end scission (depolymerization, which would be indicated by separate low-MW peaks), repolymerizing or cross-linking reactions (which would be indicated by broadening of the MWD due to the formation of high MW compounds) were not observed.

The homolytic cleavage of initiator (oxidizer) into two radicals can be written as,

$$C_2 \xrightarrow{k_p} 2C^* \tag{4}$$

The rate of disappearance of oxidizer for the above equation can be written as,

$$\frac{dc_p}{dt} = -k_p c_p \tag{5}$$

where c_p denotes the molar concentration of oxidizer. The hydrogen abstraction of the polymer chain, P(x), of molecular weight x through these radicals can be written as,

$$C^* + P(x) \xrightarrow{k_d(x)} CH + R^*(x) \tag{6}$$

The population balance equation for the consumption of oxidizer radicals can be written as

$$dc(t)/dt = 2k_p c_p(t) - c(t)\int_0^\infty k_d(x')p(x',t)dx' \tag{7}$$

The initiation and termination that occurs during polymer degradation can be written as

$$P(x) \underset{k_b}{\overset{k_a}{\rightleftharpoons}} R^*(x') + R^*(x-x') \tag{8}$$

This step is less frequent when compared with the depropagation steps and can be neglected.[17]

The reversible hydrogen abstraction from the polymer chain is

$$P(x) \underset{k_H(x)}{\overset{k_h(x)}{\rightleftharpoons}} R^*(x) \tag{9}$$

The depropagation step that occurs by the irreversible β-scission of the polymer chain is

$$R^*(x) \xrightarrow{k_s(x)} R^*(x') + P(x-x') \tag{10}$$

The population balance equations for polymer and polymer radicals can be written as

$$\partial p(x,t)/\partial t = -k_d(x)c(t)p(x,t) - k_h(x)p(x,t) + k_H(x)r(x,t) + \int_x^\infty k_s(x')r(x',t)\Omega(x,x')dx' \tag{11}$$

$$\partial r(x,t)/\partial t = k_d(x)c(t)p(x,t) + k_h(x)p(x,t) - k_H(x)r(x,t) - k_s(x)r(x,t) + \int_x^\infty k_s(x')r(x',t)\Omega(x,x')dx' \quad (12)$$

For random chain scission, the stoichiometric kernel, $\Omega(x, x')$, which determines the distribution of scission products is $1/x'$.[17] In the above expressions, the rate coefficients, k_d, k_h, k_H, and k_s, are assumed to be linearly proportional to the molecular weight.[1,2,21] Equation 5 becomes

$$dc(t)/dt = 2k_p c_p(t) - k_d p^{(1)} c(t) \quad (13)$$

The integro-differential Eqs. 11 and 12 can be converted into ordinary differential equations by the moment technique (see Appendix). The first three moments can be expressed as

$$\frac{dp^{(0)}}{dt} = k_{oxd} c(t) p^{(1)} \quad (14)$$

$$\frac{dp^{(1)}}{dt} = 0 \quad (15)$$

$$\frac{dp^{(2)}}{dt} = -\frac{k_{oxd} c(t) p^{(3)}}{3} \quad (16)$$

Equation 15 shows that $p^{(1)}$ is a constant indicating that the mass concentration of the polymer is constant throughout the reaction. For the degradation in the presence of oxidizer, the simultaneous solution of Eq. 14 along with Eqs. 5 and 13, with initial conditions $p^{(0)}(t = 0) = p_o^{(0)}$, $C_p(t = 0) = C_{po}$, and $C(t = 0) = 0$, will give the number–average molecular weight for any time (t). The analytical solution to determine number–average molecular weight, $M_n = p^{(1)}/p^{(0)}$, for thermal oxidative degradation is given by

$$\frac{M_{n0}}{M_n} - 1 = \frac{2M_{n0}c_{p0}k_{oxd}}{k_d p^{(1)}[k_p - k_d p^{(1)}]} \left(k_p(1 - e^{-k_d p^{(1)} t}) - k_d p^{(1)} \times (1 - e^{-k_p t})\right) \quad (17)$$

The above expression is used to evaluate the rate constants, k_d and k_{oxd}, by nonlinear regression of number–average molecular weight (M_n). The dissociation rate constant of BPO, k_p, is taken from the literature.[22]

The third moment, $p^{(3)}$, for the γ-distribution can be obtained as

$$p^{(3)} = p^{(1)}\beta^2(\alpha + 1)(\alpha + 2) \quad (18)$$

Substituting the above expression in Eq. 16 and using Eqs. 2 and 3, the expression for γ-distribution parameters can be written as

$$\frac{d\alpha}{dt} = \frac{2}{3} k_{oxd} c(t) M_n (1 - \alpha^2) \quad (19)$$

$$\frac{d\beta}{dt} = \frac{1}{3} k_{oxd} c(t)(2M_n^2 - 3M_n\beta - 2\beta^2) \quad (20)$$

For oxidative thermal degradation, Eqs. 19 and 20 can be solved numerically by substituting M_n from Eq. 17, using initial condition $\alpha(t = 0) = \alpha_0$ and $\beta(t = 0) = \beta_0$. Because the temperature of the reaction mixture continuously varies with time under microwave assisted oxidative degradation of polymers, the rate constants are expressed in Arrhenius form, k_0 Exp(−E/RT). For the microwave-assisted reactions, the temperature varies with time and an analytical solution similar to Eq. 17 is not possible. The temperature profile for each cycle can be written in the form of time as

$$T = \begin{cases} T_w + \frac{T_{peak} - T_w}{t_h} t & t \in (0, t_h) \\ T_{peak} - \frac{T_{peak} - T_w}{\tau - t_h}(t - t_h) & t \in (t_h, \tau) \end{cases} \quad (21)$$

where t_h is the heating time, T_w is the temperature at the end of cooling cycle, which is the same at the starting of the heating cycle, and T_{peak} is the maximum temperature reached at the end of heating cycle. The simultaneous numerical solution of Eq. 20 along with Eqs. 5 and 13 and Eqs. 19 or 20, using temperature dependency with time from Eq. 21, will give the number–average molecular weight for any time (t) and γ-distribution parameters.

Results and Discussion

The thermal oxidative degradation of PEMA was investigated at three different temperatures (60, 70, and 80°C) in the presence of BPO of initial concentration 10 g/L to compare thermal oxidative degradation and microwave-assisted oxidative degradation. Figure 2 shows the variation of number–average molecular weight of PEMA with time, and it is clear that the models fit well with experimental values. The rate constant for BPO dissociation, k_p, is given by $\ln k_p = (32.37 - 14{,}900)/T$,[23] where k_p is in s^{-1} and T is in K. The regressed values of rate coefficients for hydrogen abstraction and oxidative random chain scission are given in Table 1. The Arrhenius dependence with temperature is assumed for the rate coefficients, and the values from the Arrhenius plot

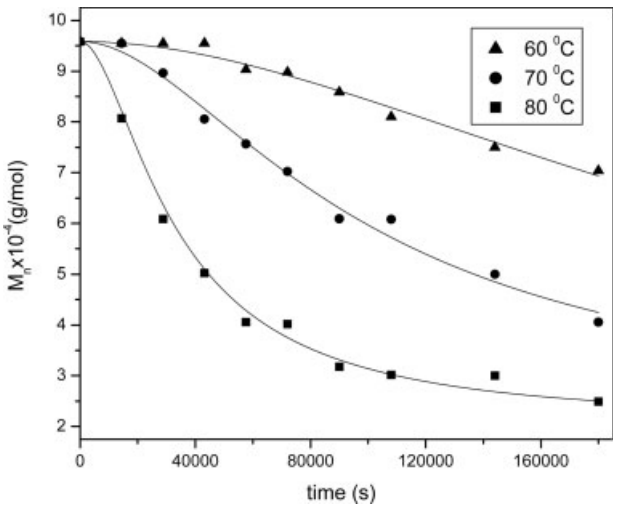

Figure 2. Variation of number–average molecular weight of PEMA under oxidative thermal degradation with time at constant initial BPO concentration of 10 g/L.

Lines are model fit.

Table 1. Rate Parameters Obtained for the Thermal Oxidative Degradation of PEMA in Presence of BPO of 10 g/L Initial Concentration

Temperature (°C)	$k_p \times 10^6$ $(s^{-1})^{23}$	$k_d \times p^{(1)} \times 10^6$ (s^{-1})	$k_{oxd} \times c_{po} \times 10^{11}$ [mol/(g s)]
60	4.2	1.71	4.10
70	15.5	5.21	7.70
80	53.2	12.40	21.26

are $\ln(k_d \times p^{(1)}) = (21.8 - 11{,}670)/T$ and $\ln(k_0 \times C_{p0}) = (4.9 - 9620)/T$, where $k_d \times p^{(1)}$ is in s^{-1}, $k_{oxd} \times C_{p0}$ is in mol/(g s), and T is in K. From Table 1, it is clear that the hydrogen-abstraction step under thermal condition is faster than the random chain scission of the polymer radical. The value of activation energy for the hydrogen-abstraction step in this study (23.4 kcal/mol) is similar to that found (25.8 kcal/mol) by Sterling et al.[2] for oxidative thermal degradation of poly(α-methylstyrene). The activation energy (19.2 kcal/mol) required for random chain scission under thermal oxidative degradation of PEMA is less than the energy required for thermal degradation in solution (25.5 kcal/mol),[19] and the rate constant value is also higher for the oxidative degradation of PEMA for the same temperature range. This confirms the enhancement in degradation in the presence of BPO. The optimized rate coefficients were substituted in Eqs. 19 and 20 and solved using *Mathematica* to determine the γ-distribution parameters with initial conditions $\alpha_0 = 4$ and $\beta_0 = 23{,}950$. The variation of γ-distribution parameters with time for thermal oxidative degradation of PEMA is shown in Figures 3a, b at three different temperatures. These γ-distribution parameters are used to simulate the MWDs as defined in Eq. 1. The experimental MWDs and simulated results are shown in Figure 4 for thermal oxidative degradation of PEMA at 70°C. Figure 4 shows the MWDs of reaction mixture for different reaction times (t = 0, 43,200, and 72,000 s). The normalized mass fraction used in the figures for MWDs is x $p(x,t)/p^{(1)}$. Figure 4 also shows the shift of MWDs toward low molecular weight region due to the degradation of polymer.

The microwave-assisted oxidative degradation of PEMA was investigated in the presence of three different oxidizers, BPO, DCP, and AIBN, for the same experimental conditions. To account for the variation of temperature of the system with time, the rate coefficients were expressed in Arrhenius form as $k_p = k_{p0}\exp(-E_p/RT)$, $k_d = k_{d0}\exp(-E_d/RT)$, and $k_{oxd} = k_{oxd0}\exp(-E_{oxd}/RT)$, and the temperature in the rate coefficients was substituted in the form of time from Eq. 21. The dissociation rate constants of the initiators were taken from the literature.[22,23] The rate parameters for hydrogen abstraction and oxidative random chain scission were used as model fitting parameters. The model is first tested for the degradation in the presence of BPO. The rate parameters were substituted in the governing Eqs. 5,13,14, and 20 and solved using *Mathematica*. The regressed values of $k_d \times p^{(1)}$

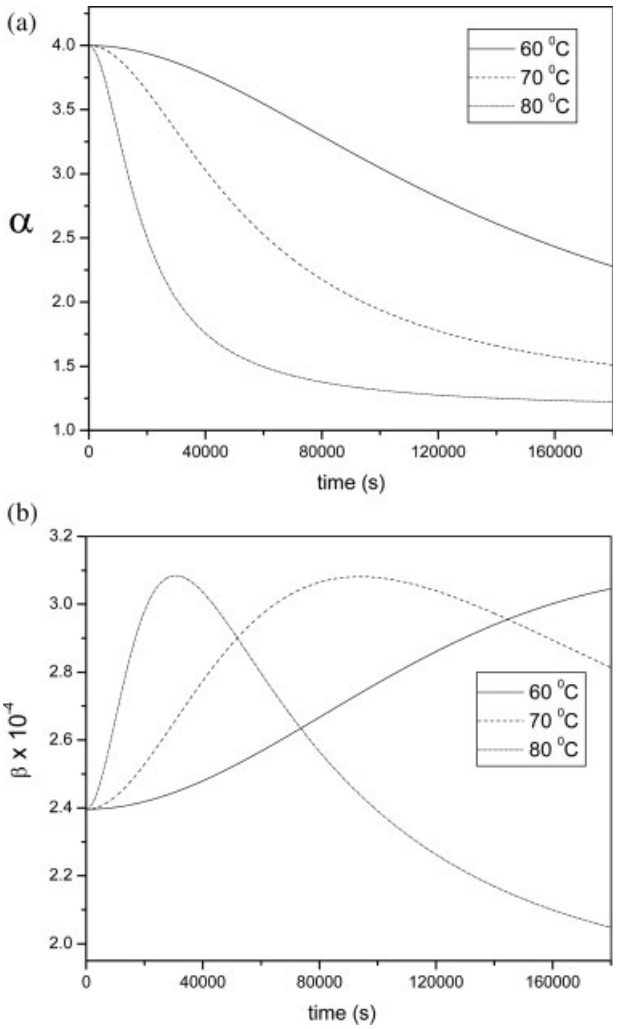

Figure 3. Variation of γ-distribution parameter (a) α and (b) β with time for oxidative thermal degradation of PEMA at constant initial BPO concentration of 10 g/L.

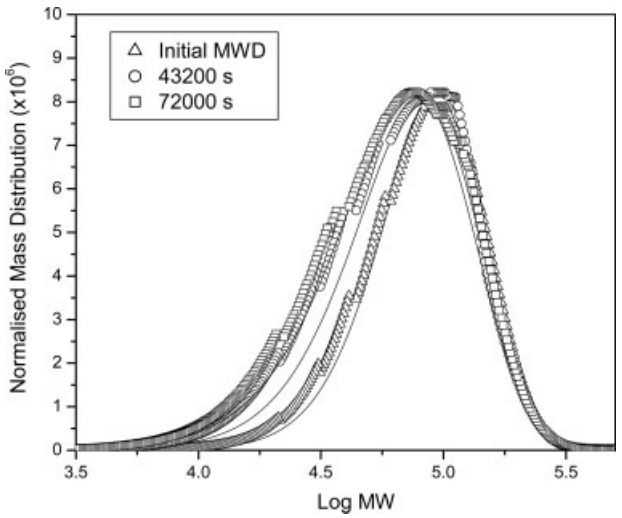

Figure 4. MWDs for the oxidative thermal degradation of PEMA at 70°C for different reaction times (t = 0, t = 43,200 s, and t = 72,000 s).

Lines are simulated values from γ-distribution.

Table 2. Rate Parameters Obtained for Microwave-Assisted Oxidative Degradation of PEMA with Various Oxidizers

Oxidizer	$\ln k_p$	$\ln k_d \times p^{(1)}$	$\ln k_{oxd} \times c_{po}$
BPO	$(32.37 - 14{,}900)/T^{23}$	$(15.0 - 5000)/T$	$(15.5 - 7000)/T$
AIBN	$(35.00 - 15{,}900)/T^{23}$	same as above	same as above
DCP	$(38.38 - 19{,}100)/T^{22}$	same as above	same as above

k_p and $k_d \times p^{(1)}$ are in s^{-1}, $k_{oxd} \times C_{p0}$ is in mol/(g s), and T is in K.

and $k_{oxd} \times c_{p0}$ are given in Table 2. The same values of $k_d \times p^{(1)}$ and $k_{oxd} \times c_{p0}$, obtained for degradation in the presence of BPO, are used for simulating the results for the degradation in the presence of AIBN and DCP by substituting the corresponding dissociation rate constant values (k_p) of the oxidizers in the governing equations. The simulated results for the prediction of number–average molecular weight (M_n) are in good agreement with the experimental values (Figures 5a, b). It is clear that by calculating the values of $k_d \times p^{(1)}$ and $k_{oxd} \times c_{p0}$ (which are dependent only on nature of the polymer) from the polymer degradation in the presence of any one of the initiators, the above model can be used to predict the degradation rates in the presence of any other initiators by knowing only the rate constant values (k_p) of the oxidizers, which can be taken from the literature. This is due to the observation that the hydrogen abstraction and oxidative random chain scission rate coefficients are independent of the oxidizer. Similar results were observed by Ikeda et al.[24] for the hydrogen abstraction from polymer by oxidizer radicals (Eq. 11) for the oxidative degradation of poly(methyl styrene) initiated by photodecomposition of AIBN. Thus, the overall degradation rate of the polymer will be comparatively faster in the presence of oxidizing agent of faster dissociation rate. Figures 5a, b show the variation of number–average molecular weight of PEMA with time at constant heating time of 70 and 100 s, respectively, and at constant initial oxidizer concentration of 10 g/L for BPO, DCP, and 5 g/L of AIBN. From Figure 5b, it can be seen that for the same oxidizer concentration of 10 g/L, the degradation of PEMA is faster in the presence of BPO than that of DCP. This is due to the faster dissociation rate of BPO. In all the experiments, the trend is clear that the polymer degradation is in the order of BPO > AIBN > DCP. The variation in molecular weight in steps with time (Figures 5a, b) is due to the alternative heating and cooling for one complete cycle. Thus, the molecular weight of the polymer decreases rapidly during the heating cycle and slowly during the cooling cycle.

To investigate the effect of heating time (t_h) on the overall degradation rate, the degradation of PEMA was studied at four different heating times (60, 70, 80, and 100 s) in the presence of BPO of constant initial concentration 10 g/L. Figure 6 shows the variation of number–average molecular weight with time for different heating time. The symbols represent experimental data, and lines are the model prediction.

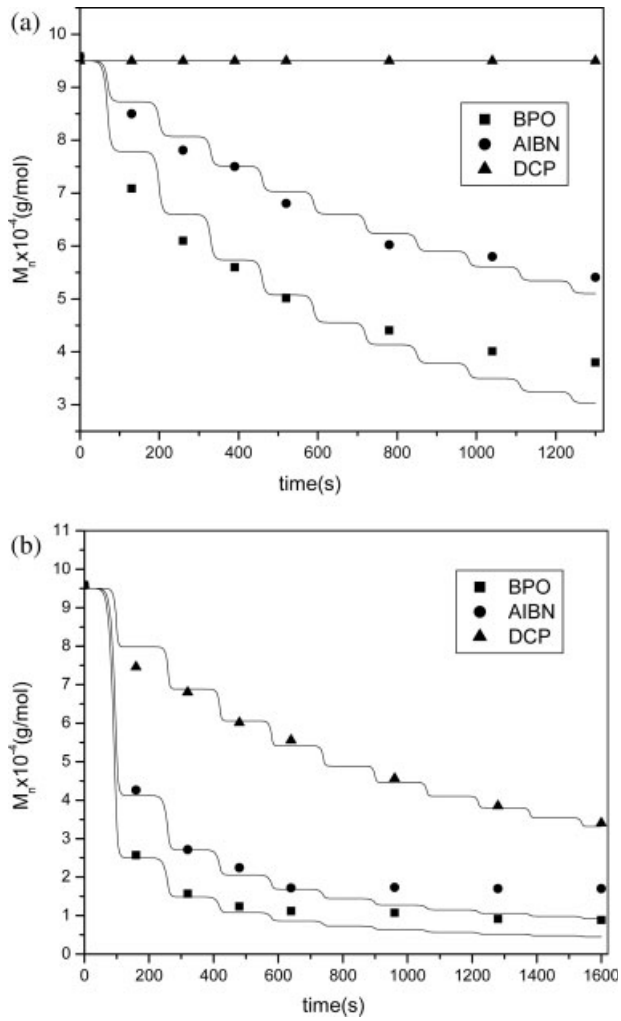

Figure 5. Variation of number–average molecular weight of PEMA under microwave-assisted oxidative degradation with time (a) for constant heating time of 60 s and (b) for constant heating time of 100 s and BPO initial concentration of 10 g/L.

Lines are model fit.

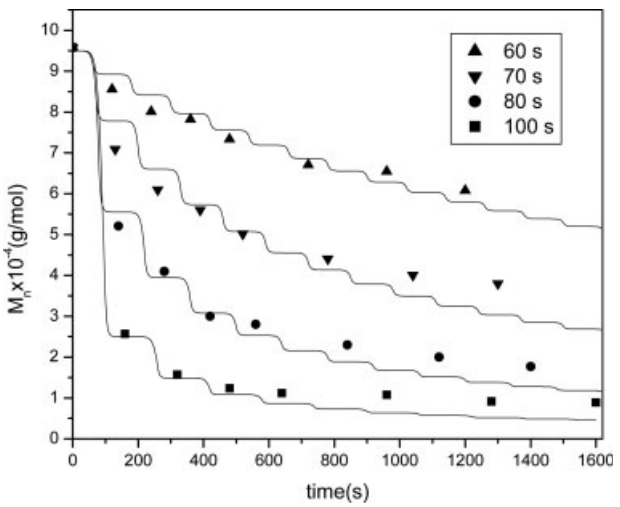

Figure 6. Variation of number–average molecular weight of PEMA under microwave-assisted oxidative degradation with time for different heating times in presence of BPO of initial concentration of 10 g/L.

Lines are model fit.

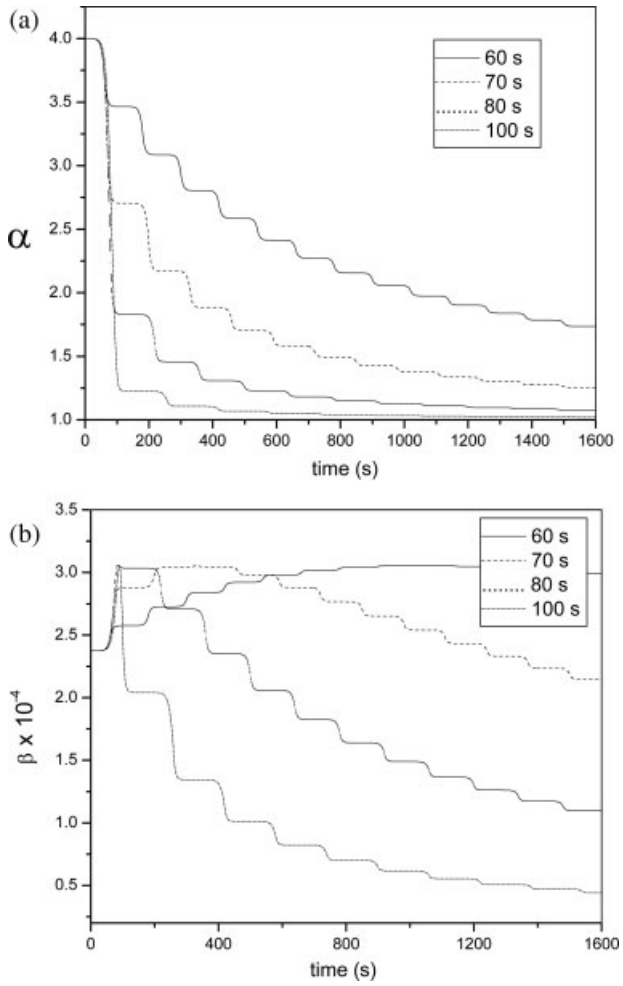

Figure 7. Variation of γ-distribution parameters with time (a) α and (b) β for microwave-assisted oxidative degradation of PEMA at different heating times in presence of BPO of initial concentration of 10 g/L.

At high heating time (100 s), the number–average molecular weight decreases rapidly at the end of the first cycle. The degradation observed in subsequent cycles is very slow. This can be attributed to almost a complete consumption of the oxidizer in the first cycle itself. However, in case of lower heating time (60 s), the oxidizer is consumed gradually in each cycle, and the molecular weight decreases in each cycle. Thus, the overall degradation of the polymer depends on the number of cycles, especially for the lower heating time per cycle. Figures 7a, b show the variation of γ-distribution parameters with time for microwave-assisted oxidative degradation of PEMA with 60 s heating time (t_h) in the presence of BPO of initial concentration of 10 g/L. From the figure, it is clear that α approaches unity in all cases. At lower heating time (t_h), the approach to unity is longer. Thus, the MWDs approach an exponential distribution in all cases. For the oxidative degradation of polystyrene in solution, it was observed that if the initial distribution was exponential, then the MWD remains as an exponential distribution (PD of two) throughout the reaction time, although the average molecular weight decreases.[3] In this study, it is observed that, irrespective of the initial MWD, the distribution approaches an exponential distribution for the oxidative degradation of PEMA under both thermal (Figures 3a, b) and microwave-assisted oxidative degradation (Figures 7a, b). Similar results have also been observed[18] for nonoxidative degradation of polymers that degrade by random chain scission only. From Figure 7b, it is observed that β goes through maximum for some cases. This is to compensate the decrease in the number–average molecular weight (M_n), because α decreases more than M_n with time. Figures 7a, b show that both α and β changes at initial times; however, after α approaches unity, β varies continuously with time. These γ-distribution parameters are used to simulate the MWD as defined in Eq. 1. Figures 8a, b show the MWDs for the microwave-assisted oxidative degradation of PEMA at 60-s heating time in the pres-

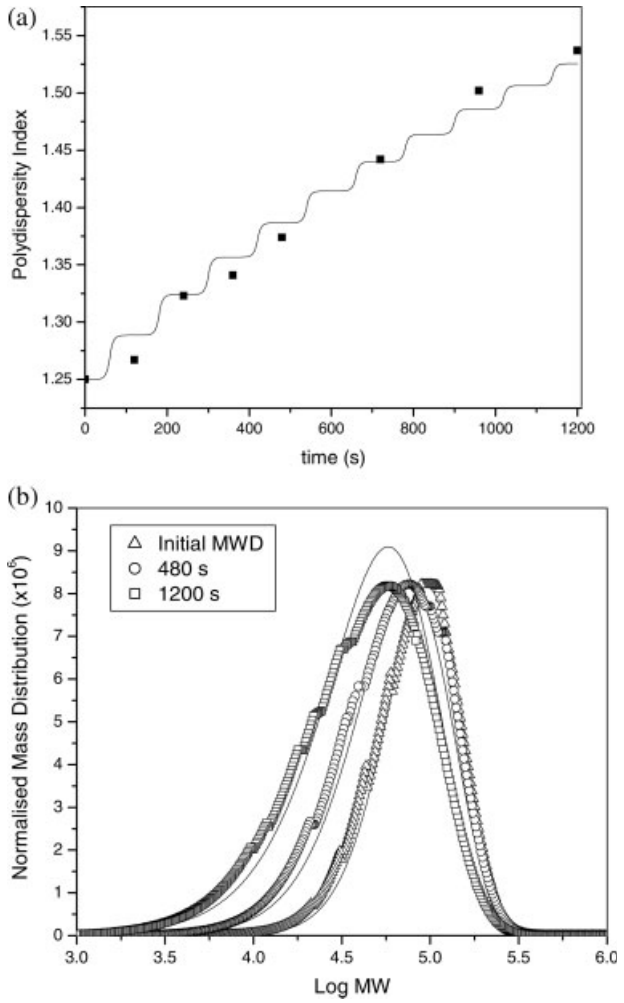

Figure 8. (a) Variation of polydispersity with time for microwave-assisted oxidative degradation of PEMA at 60 s heating time in presence of BPO of initial concentration of 10 g/L; (b) MWDs under microwave-assisted oxidative degradation of PEMA for 60 s heating time at different reaction times (t = 0, 480 and 1200 s). Lines are simulated values from γ-distribution.

Lines are model fit.

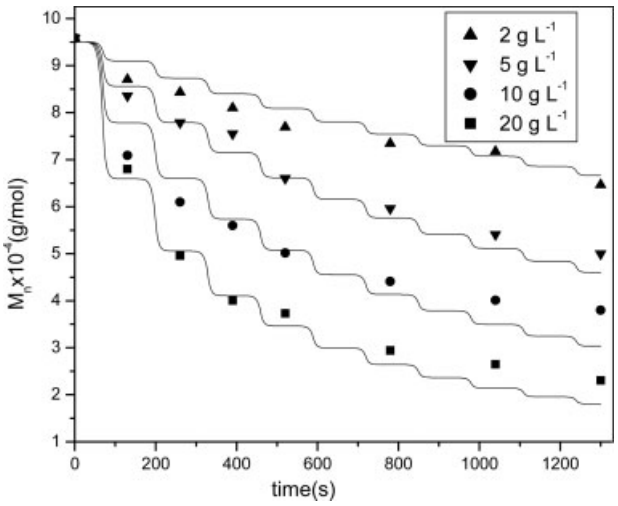

Figure 9. Variation of number–average molecular weight of PEMA under microwave-assisted oxidative degradation with time for 70 s heating time in presence of BPO of different initial concentration (g/L).

Lines are model fit.

ence of BPO of initial concentration 10 g/L. Figure 8a confirms the continuous increasing trend of polydispersities with time from the initial value (1.25) to approach a value of 2. The simulated results for polydispersities are in good agreement with the experimental data. Figure 8b shows the MWDs for the degradation of 60-s heating time at different reaction times (t = 0, 480, and 1200 s). The generalized γ-distribution predicts the experimental data.

The effect of concentration of oxidizer on the overall degradation rate was investigated by conducting the degradation of PEMA at 70-s heating time with different initial concentrations of BPO (2, 5, 10, and 20 g/L). Figure 9 shows the variation of number–average molecular weight of PEMA with time at different BPO initial concentrations. A significant decrease in number–average molecular weight of the polymer is observed with an increase in oxidizer concentration. At higher oxidizer concentration, larger amounts of oxidizer radicals degrade the polymer leading to a significant decrease in the polymer molecular weight.

The effect of alkyl group substituents on the overall polymer degradation was investigated by studying the degradation of PMMA, PEMA, and PBMA in the presence of 10 g/L of initial BPO concentration at two different heating times (70 and 100 s). Figures 10a, b show the variation of number–average molecular weights of PEMA, PBMA, and PMMA, respectively, with time for two different heating times. The regressed rate coefficient values for hydrogen abstraction and oxidative random chain scission are given in Table 3. From Figure 10a, it is clear that PBMA degrades faster than PEMA. Table 3 shows that both rate coefficients,-the hydrogen abstraction and the oxidative random chain scission, increases with increase in alkyl group and the degradation rate follows the order, PBMA > PEMA > PMMA. It is expected that the hydrogen abstraction increases in the order of primary < secondary < tertiary, and the order is

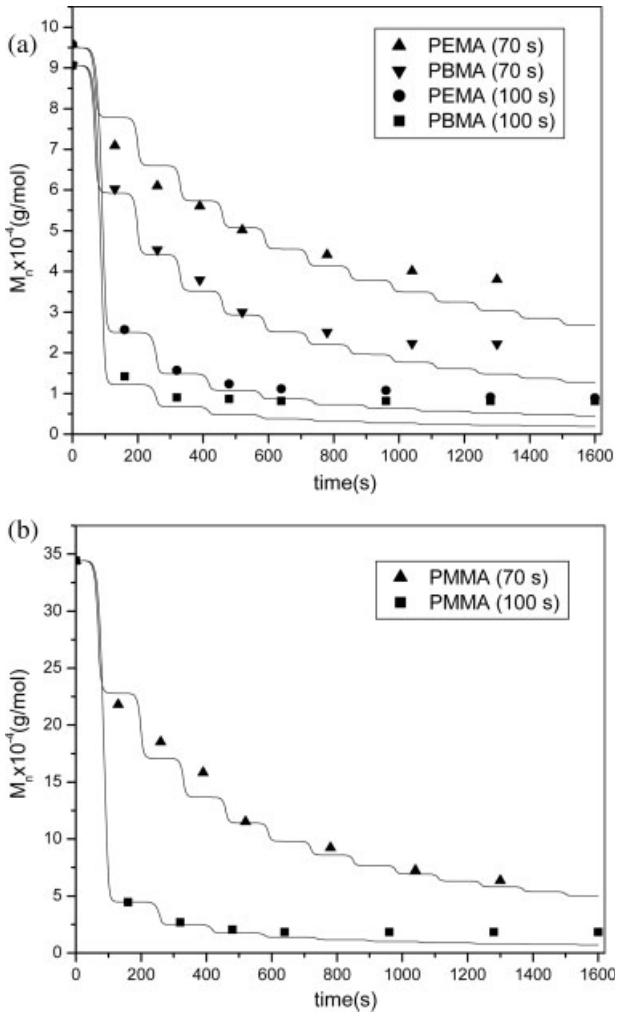

Figure 10. Variation of number–average molecular weight of PAMA under microwave-assisted oxidative degradation with time (a) for PEMA and PBMA (b) for PMMA at two different heating times in presence BPO of initial concentration 10 g/L.

independent of the nature of attacking radical.[24] Thus, the amount of peroxide radical produced from Eq. 4 is same for the degradation of three polymers, but the peroxide radical consumption in Eq. 6 to produce polymer radical depends on the nature of the polymer and it is fastest for PBMA. The increase in chain scission rate with chain length can be attributed to the steric factor of the larger alkyl chain in the methacrylates.[25] A similar trend has been reported[19] for

Table 3. Rate Parameters Obtained for Microwave-Assisted Oxidative Degradation of PMMA, PEMA, and PBMA in the Presence of BPO of 10 g/L Initial Concentration

Polymer	ln k_p[23]	ln $k_d \times p^{(1)}$	ln $k_{oxd} \times c_{po}$
PMMA	32.37 − 14,900/T	14.6 − 5400/T	15.2 − 7600/T
PEMA	32.37 − 14,900/T	15.0 − 5000/T	15.5 − 7000/T
PBMA	32.37 − 14,900/T	15.2 − 4600/T	15.8 − 6300/T

k_p and $k_d \times p^{(1)}$ are in s^{-1}, $k_{oxd} \times C_{p0}$ is in mol/(g s) and T is in K.

the degradation of poly(alkyl methacrylates) under both pyrolysis and thermal degradation in solution. The activation energies for the microwave-assisted oxidative degradation of PMMA, PEMA, and PBMA were 15.2, 14.0, and 12.6 kcal/mol, respectively, and thus the activation energy decreased with length of alkyl group. Comparing the degradation of PEMA under different experimental conditions, the activation energy required for the random chain scission are in the order of pyrolysis (36.1 kcal/mol)[19] > thermal degradation in solution (25.5 kcal/mol)[19] > oxidative thermal degradation (19.2 kcal/mol) > microwave-assisted oxidative degradation (14.0 kcal/mol). The values of rate constants are also in the reverse order and confirm the enhancement in degradation rate under microwave-assisted condition.

Conclusions

The microwave-assisted oxidative degradation of PEMA was compared to thermal oxidative degradation, and the results show the enhancement in degradation rate under microwave heating. The initial MWD of polymer was expressed as γ-distribution, and the mathematical solutions for any time (t) were developed in terms of time-dependent γ-distribution parameter. The parameter, α, of γ-distribution approached unity, and thus the MWD reaches an exponential distribution. The degradation of PEMA was investigated in the presence of three different oxidizers. The differences in the overall degradation rate of poly(ethyl acrylate) in the presence of different oxidizing agents were only dependent on the rate of oxidizer dissociation. The model developed can be used to predict degradation rate of the polymer in the presence of any oxidizers by knowing only its dissociation rate constant values. The microwave-assisted oxidative degradation rate of poly(alkyl methacrylates) increased with increase in the number of carbon atom of the alkyl substituents, followed the order PBMA > PPMA > PEMA > PMMA, and the activation energy decreased with chain length.

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Appendix: Derivation for moments

Applying moment operation on Eqs. 9 and 10,

$$\frac{dp^{(j)}}{dt} = -k_d c(t) p^{(j+1)}(t) - k_h p^{(j+1)} + k_H r^{\cdot(j+1)} + \frac{k_s}{j+1} r^{\cdot(j+1)} \tag{A1}$$

$$\frac{dr^{(j)}}{dt} = k_d c(t) p^{(n+1)}(t) + k_h p^{(j+1)} - k_H r^{\cdot(j+1)} - k_s \frac{j}{j+1} r^{\cdot(j+1)} \tag{A2}$$

The quasi-steady state approximation (QSSA) can be applied because of the small number of radicals and, therefore, resulting in a negligible change of the radical MWDs with time compared to variations of the polymer molecular weight distribution. A previous work[26] has examined the consequences of the QSSA by solving the equations numerically and found that QSSA only slightly alters the initial time dependence of the polymer concentration and is valid in

most cases of polymer degradation. Applying QSSA to the polymer radicals, Eq. A2 can be written as

$$r^{(j+1)} = (j+1)p^{(j+1)}\frac{k_d c(t) + k_h}{jk_s + (j+1)k_H} \tag{A3}$$

The simultaneous solution of Eqs. A1 and A3 gives the jth moment as

$$\frac{dp^{(j)}}{dt} = -(j-1)k_s\frac{k_d c(t) + k_h}{jk_s + (j+1)k_H}p^{(j+1)} \tag{A4}$$

The above expression is the general expression for jth moment. By substituting $j = 0$, 1, and 2, the expression for first three moments can be obtained to determine γ-distribution parameters. For $j = 1$, Eq. A4 becomes

$$\frac{dp^{(1)}}{dt} = 0 \tag{A5}$$

For $j = 0$, the molar concentration of polymer from Eq. A4 is

$$\frac{dp^{(0)}}{dt} = k_0 p^{(1)} \tag{A6}$$

where the overall rate coefficient k_0 is given by $k_{oxd}c(t) + k_t$. The oxidative degradation coefficient, k_{oxd}, is $k_d k_s/k_H$ and the degradation coefficient in the absence of oxidizer, k_t, is $k_h k_s/k_H$. Because there was no degradation observed in the absence of oxidizer for the same temperature range,[19] the overall rate coefficient (k_0) can be written as $k_0 \approx k_{oxd}c(t)$. Thus Eq. a6 becomes

$$\frac{dp^{(0)}}{dt} = k_{oxd}c(t)p^{(1)} \tag{A7}$$

For $j = 2$, Eq. A4 becomes

$$\frac{dp^{(2)}}{dt} = -k_s\frac{k_d c(t) + k_h}{2k_s + 3k_H}p^{(3)} \tag{A8}$$

The hydrogen abstraction of polymer radicals is expected to be much faster than its scission,[1,2] that is, $k_H \gg k_s$, Eq. A8 becomes

$$\frac{dp^{(2)}}{dt} = -\frac{k_{oxd}c(t)p^{(3)}}{3} \tag{A9}$$

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