

Continuous distribution kinetics for oxidative degradation of PMMA in solution

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Abstract

The oxidative degradation of poly(methyl methacrylate) (PMMA) was investigated in chlorobenzene at 50–100°C for various peroxide and polymer concentrations. Unlike thermal degradation, the chain scission of PMMA occurs randomly across the polymer backbone. The samples were analyzed by gel permeation chromatography (GPC) to obtain the time evolution of molecular weight distributions (MWDs). A continuous distribution model for polymer degradation and simultaneous peroxide deactivation was developed assuming that the rate coefficients depend linearly on MW. This model was used to determine the rate coefficients for the oxidative degradation of PMMA. The activation energy, determined from the temperature dependence of the rate coefficients, was 48.2 kcal/mol. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Oxidative degradation; Random chain scission; Poly(methyl methacrylate); Rate coefficients; Radical mechanisms

1. Introduction

In the recent years, considerable effort has been devoted to the study of polymer degradation. In general, degradation of polymers can be accomplished by various methods like heat, light, mechanical stresses and oxidizing agents [1–3]. The study of oxidative degradation of polymers is interesting both from theoretical and practical standpoints. Unlike thermal degradation, where the polymer scission can occur randomly [4] and/or at the chain-end [5], oxidative degradation is interesting because the scission in the polymer backbone occurs only randomly. The addition of free radical initiators to polyolefins during extrusion is used industrially to improve mechanical properties of the polymer [6]. Polymer degradation by adding peroxide is a common manufacturing technique [7] because the controlled addition of peroxide to polypropylene leads to polymers with superior flow properties [6,8]. Addition of peroxide during the extrusion of polyethylene leads to increase in the durability of the polymer [9]. Other studies include addition of peroxides to blends of polyolefins and rubber [10] to improve the

mechanical properties. The improved properties are due to the change in the polymer MWD caused by the reaction with peroxide.

Kamiya and Niki [11], in their review of oxidative degradation of polymer, mention that the kinetics and mechanisms are complex. Many investigations of polymer degradation have centered on determining the yield of monomer and the rate of change of average molecular weight. Continuous distribution kinetics can provide more details of the degradation process by accounting for the time evolution of the complete MWD. Continuous kinetics has been used to study the thermo-oxidative degradation of polystyrene in solution [12] but the energy of activation was not evaluated. In a subsequent study, Kim and McCoy [13] have determined the energy of activation for the oxidative degradation of polystyrene.

Degradation of polymers in solution is favorable since there is only a single phase, good temperature control and enhancement in the reaction rates leading to degradation at lower temperatures compared to pyrolysis [14]. Oxidative degradation of the polymer occurs at temperatures much lower than conventional pyrolysis, thus resulting in considerable energy savings.

In this study, we present experimental data of the oxidative degradation of PMMA in solution. The

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objective of present work is to study the oxidative degradation of PMMA in chlorobenzene at various temperatures and at various concentrations of the polymer and peroxide. The experimental data evince that the degradation of the polymer and the deactivation of initiator occur simultaneously. We propose a continuous distribution kinetics model for the oxidative degradation of PMMA that accounts for concurrent chain scission of the polymer and the deactivation of the peroxide. The MWDs are analyzed with the theoretical model to obtain rate parameters for chain scission. The activation energy for the chain scission is determined from the temperature dependence of the rate coefficient.

2. Experimental

2.1. Materials

The methyl methacrylate monomer, benzoyl peroxide and chlorobenzene were obtained from S. D. Fine Chemicals. The monomer was freed from the phenolic inhibitor (4-*tert*-butylcatechol) by washing with 10% sodium hydroxide solution, followed by washing with distilled water. Benzoyl peroxide was purified by dissolving in chloroform and precipitating it in a non-solvent, methanol.

2.2. Oxidative degradation

PMMA ($M_n = 240\,000$; $M_w = 380\,000$) was made by bulk polymerization with benzoyl peroxide as the initiator at 60°C. The oxidative degradation of PMMA was carried out in a three-neck round-bottomed flask with continuous stirring at various temperatures (50–100°C). No reaction was observed at these temperatures in the absence of peroxide. The temperature was controlled to within 2% of set point with an on-off controller (thermotherm). The reactor was charged with 100 ml of chlorobenzene and the temperature of the solution was raised to the reaction temperature. The polymer concentration was varied from 2 to 30 g/l and the initiator concentration was varied from 1.5 to 10 g/l. Samples of 1 ml were taken at regular intervals for subsequent analysis. The samples were quenched in cold water to avoid any further reaction.

2.3. GPC analysis

The samples are analyzed with GPC at 40°C with the eluent THF (Merck) at a flow rate of 1 ml/min. The GPC consists of three gel columns of different pore sizes and an online refractive index detector. The chromatograph is obtained as a plot of retention time (every 0.1 s) versus refractive index. The obtained chromatograph was converted to MWDs with a calibration curve,

reported in our earlier study [15]. As shown in Fig. 1, no specific products were formed and all polymer degraded by random chain scission.

3. Theoretical model

We consider the dynamics of the reaction system such that it accounts for the decrease in peroxide concentration as well as for the degradation of the polymer. The peroxide dissociates into two radicals with a rate coefficient of k_p ,



This radical abstracts hydrogen atoms from the polymer $P(x)$ forming radicals $R^\bullet(x)$ with a rate coefficient, $k_d(x)$,



This reaction neutralizes the peroxide radical. The mass balance of the peroxide radical can be written, assuming that the dissociation is extremely fast, as [13]

$$dc/dt = -c(t) \int_0^\infty k_d(x')p(x', t)dx' \quad (1)$$

The rate coefficient, $k_d(x)$, of reaction (B) can be assumed to be proportional to MW, $k_d(x) = k_d x$. Moments, defined by $\int_0^\infty x^n [] dx$, can be operated on Eq. (1) to yield,

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

The polymer radical undergoes thermal initiation and termination given by

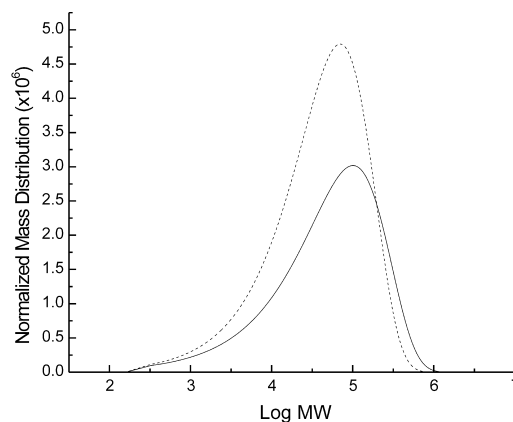
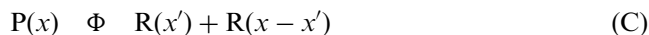


Fig. 1. Time evolution of MWD for the oxidative degradation of PMMA at $c_0/p^{(1)} = 2 \times 10^{-4}$ mol/g at 170°C. Experimental data points are smoothed by a cubic spline. Legend: — initial distribution; - - - final distribution.



The rates of this reaction can be neglected based on the long-chain approximation [16]. The polymer radical may abstract hydrogen from a polymer and this reaction can be represented as a reversible interchange of a polymer to a radical [16],



The polymer radicals undergo irreversible β -scission, and this reaction is represented by



The governing population balance equation for the polymer and radical by reactions, (B), (C), (D) and (E) in a batch reactor can be expressed as [4,13],

$$\begin{aligned} \frac{\partial p(x, t)}{\partial t} = & -k_d(x)c(t)p(x, t) + c(t) \int_x^\infty k_b(x')r(x', t) \\ & \Omega(x, x')dx' - k_h(x)p(x, t) + k_{hr}(x)r(x, t) \end{aligned} \quad (3)$$

$$\begin{aligned} \frac{\partial r(x, t)}{\partial t} = & k_d(x)c(t)p(x, t) - k_b(x)r(x, t) + \int_x^\infty k_b(x') \\ & r(x', t)\Omega(x, x')dx' + k_h(x)p(x, t) - k_{hr}(x)r(x, t) \end{aligned} \quad (4)$$

The stoichiometric kernel in Eqs. (3) and (4) accounts for the type of fragmentation of a molecule of MW x to x' and $x-x'$. The degradation of PMMA is purely by random chain scission and the stoichiometric kernel can be expressed as $1/x'$ [17]. The rate coefficients, k_{hr} , k_h and k_b , of reactions (D) and (E), are assumed to depend linearly on the MW, x . Operating moments on Eqs. (3) and (4) yields,

$$\begin{aligned} \frac{dp^{(n)}}{dt} = & -k_dc(t)p^{(n+1)} + k_b r^{(n+1)}/(n+1) - k_h p^{(n+1)} \\ & + k_{hr} r^{(n+1)} \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{dr^{(n)}}{dt} = & -k_dc(t)p^{(n+1)} - k_b n r^{(n+1)}/(n+1) + k_h p^{(n+1)} \\ & - k_{hr} r^{(n+1)} \end{aligned} \quad (5a)$$

For $n=1$, Eq. (5) and (5a) can be added to yield, $d(p^{(1)} + r^{(1)})/dt = 0$. This confirms the mass balance of the system. The quasi steady-state approximation [16] suggests that the change in radical concentration is negligible, i.e. $dr^{(n)}/dt = 0$. Based on this approximation, Eq. (5a) is equated to zero and the resulting Eq. 5 can be written as

$$\begin{aligned} \frac{dp^{(n)}}{dt} = & (k_dc(t) + k_h)k_b(1 - \ln) \\ & [n - k_b + k_{hr}(n+1)]^{-1} p^{(n+1)} \end{aligned} \quad (6)$$

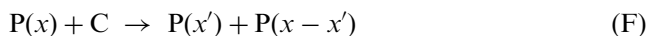
It is reasonable to assume that the hydrogen abstraction rate exceeds the rate of chain scission [13] and thus, $n k_b \gg k_{hr}(n+1)$ and this reduces Eq. (6) to

$$\frac{dp^{(n)}}{dt} = -A k_{rs} p^{(n+1)} \quad (7)$$

where $A = (n-1)/(n+1)$, $k_{rs} = k_s c(t) + k_r$, $k_s = k_d k_b k_{hr}^{-1}$ and $k_r = k_h k_b k_{hr}^{-1}$. When no peroxide is present in the system, $k_{rs} = k_r$ the exact expression derived earlier by Kodera and McCoy [16] for the non-oxidative random degradation of polymers. No reaction occurs in the absence of peroxide at the investigated temperatures. Thus, when peroxide is present in the system, $k_s c(t) \gg k_r$, and Eq. (7) reduces to

$$\frac{dp^{(n)}}{dt} = -A k_s c(t) p^{(n+1)} \quad (8)$$

Eqs. (2) and (8) are the same expressions derived by considering an overall model for oxidative degradation of polymers [12],



Here, reactions (F) and (G) represent the chain scission and peroxide deactivation reactions, with rate coefficients, $k_s(x)$ and $k_d(x)$, respectively. A mathematical solution to Eqs. (2) and (8) can be obtained by defining a new variable, θ , such that

$$d\theta = k_s c(t) dt \quad (9)$$

Eq. (8) becomes

$$\frac{dp^{(n)}}{d\theta} = -A p^{(n+1)} \quad (10)$$

The first two moments for the polymer MWD can be written from Eq. (10)

$$\frac{dp^{(0)}}{d\theta} = p^{(1)} \quad (11)$$

$$\frac{dp^{(1)}}{d\theta} = 0 \quad (11a)$$

Eq. (11a) indicates that $p^{(1)}$ is constant ($= p_0^{(1)}$) i.e. mass of the polymer is conserved. Solving Eq. (11) with the initial condition, $p^{(0)}(t=0) = p_0^{(0)}$, yields,

$$p^{(0)} - p_0^{(0)} = p^{(1)} \theta \quad (12)$$

The number-average molecular weight, M_n , of the polymer is defined as $p^{(1)}/p^{(0)}$. Eq. (8), therefore, can be rewritten as,

$$M_n^{-1} - M_{n0}^{-1} = \theta \quad (13)$$

Eq. (13) depicts the variation of the number-average MW with θ .

4. Results and discussion

We studied the degradation of PMMA at various temperatures with several initiator and polymer concentrations. The degradation rate coefficients were determined by analyzing the MWDs at various reaction times. We observed that all the reaction took place within the first 30 min indicating that the peroxide is consumed within this period. This is consistent with the results of Madras and McCoy [12], who observed that all the peroxide was depleted within the first 15 minutes and the final MWD was reached in this time. Fig. 1 shows the initial and final MWD. Eq. (9) can be written for the final time, θ_f wherein the final number average MW, M_{nf} , is reached,

$$M_{nf}^{-1} - M_{n0}^{-1} = \theta_f \quad (14)$$

Eliminating dt in Eq. (2) with Eq. (9),

$$d\theta = -k_s dc / (k_d p^{(1)}) \quad (15)$$

Integration from the initial condition, $\theta = 0$, $c = c_0$ to the final condition, $\theta = \theta_f$, $c = 0$, yields,

$$\theta_f = k_s c_0 / (k_d p^{(1)}) \quad (16)$$

Eq. (16) combined with Eq. (14) yields,

$$M_{nf}^{-1} - M_{n0}^{-1} = k_s c_0 / (k_d p^{(1)}) \quad (17)$$

This indicates that a plot of $(M_{nf}^{-1} - M_{n0}^{-1})$ versus $c_0/p^{(1)}$ would yield a slope of k_s/k_d , i.e. the slope of the plot is just the ratio of the rate coefficients of the chain scission and peroxide deactivation, represented by the overall reactions (F) and (G).

Fig. 2 shows the variation of θ_f with $c_0/p^{(1)}$ for various temperatures. Within experimental error, the theory fits the experimental data satisfactorily. The ratio of the rate coefficients, determined from the slope of the plot, was 8.35×10^{-5} , 2.08×10^{-4} and 8.38×10^{-3} at 50, 75 and 100°C, respectively. The rate coefficient of the chain scission was determined by multiplying the ratio of the rate coefficients with the rate coefficient of peroxide deactivation, determined from the literature [18]. The activation energy of chain scission was determined from the temperature dependence of the rate coefficient. The activation energy, determined from the slope of Fig. 3, is 48.2 kcal/mol.

The activation energies for a general polymer undergoing non-oxidative random chain scission are dependent upon the activation energies for reactions (D) and

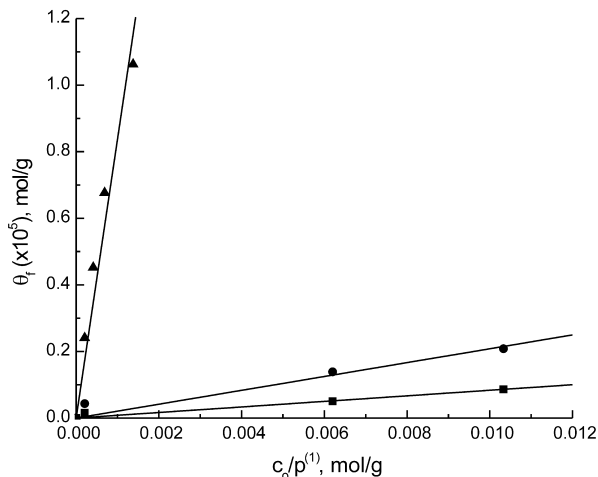


Fig. 2. Plot of θ_f versus $c_0/p^{(1)}$ to determine the ratio of the rate coefficients. Legend: ■ -50°C; ● -75°C; ▲ -100°C.

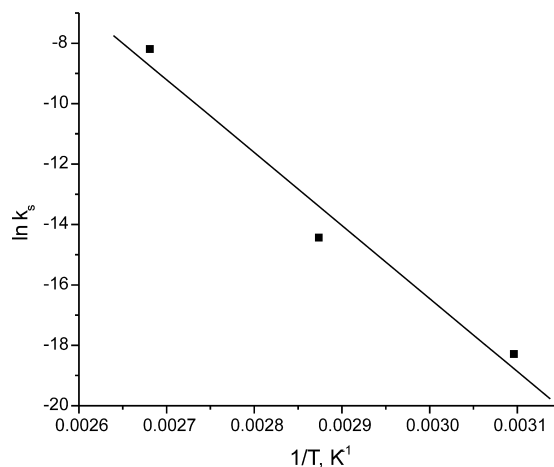


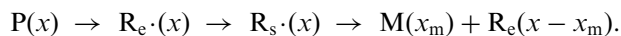
Fig. 3. Arrhenius plot to determine the energy of activation of the scission rate coefficient.

(E) [16]. The activation energy for reaction (E) is $E_b (= 29$ kcal/mol [16]) and for reaction (D) is $E_b (= 8$ kcal/mol [16]) and thus the overall activation energy is 37 kcal/mol. Depending on the type of the polymer, the activation energies vary but are generally in the range of 25–50 kcal/mol. The activation energy obtained in this study is comparable to the activation energies of 38 and 25 kcal/mol reported in the literature for the non-oxidative thermal random chain scission of poly(styrene-allyl alcohol) [4,19] and LDPE in solution [20], respectively.

It is not possible to compare this activation energy with that of the thermal non-oxidative degradation of PMMA in solution because the polymer degrades thermally by chain-end scission yielding the monomer [21]. This phenomenon of a polymer undergoing chain-end scission in thermal degradation and undergoing random chain scission during oxidative degradation has been observed for poly(α -methyl styrene). This polymer

degrades randomly during oxidative thermolysis because a secondary hydrogen is abstracted from the backbone of the main chain [22].

The chain end scission of the polymer, $P(x)$, to yield a monomer M of MW x_m occurs by three main steps [16],



with rate coefficients of k_{he} , k_{ih} and k_{bs} , respectively. The activation energies for the chain end scission of the polymer are generally in the range of 8–15 kcal/mol [16,19]. The activation energy for the thermal chain-end degradation of PMMA to its monomer is 8 kcal/mol [21]. The activation energy obtained in this study confirms that the oxidative degradation of PMMA is by random chain scission while the thermal non-oxidative degradation of PMMA is by chain-end scission.

5. Conclusions

The oxidative degradation of PMMA was studied with at different temperatures with varying concentrations of the initiator and polymer. The samples were analyzed by gel permeation chromatography and the time evolution of the MWDs was determined. A continuous distribution kinetic model that accounts for random chain scission of the polymer and peroxide activation was proposed. The rate coefficients were assumed to be linearly dependent on the MW. The rates for peroxide deactivation and polymer decomposition were assumed to be first order in polymer and peroxide concentrations. The experimental data were fitted to the model and the rate coefficients were determined. The activation energy for the random chain scission for the oxidative degradation was determined from the temperature dependence of the rate coefficient.

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