

Heat and radiation effect on the degradation behaviors of polymeric liquids

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Abstract

We propose a mathematical model based on continuous-mixture kinetics to describe the degradation mechanism of polymeric material. Chu's distribution function is employed to represent molecular-weight distributions of decomposed polymers. Calculated results agree fairly well with experimental observations for polymer degradation. The radiation damage is demonstrated as a number of chain scissions caused and G value for the scission that is defined as a number of radiolysis events caused by the absorption of 100 eV of radiation.

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1. Introduction

Degradation is an important aspect of polymer science and can be helpful in studying the feasibility of plastics recycling and in characterizing polymeric structure [1,2].

Polymer degradation occurs mainly due to the macromolecular chain scission under the various effects such as thermal, biological, mechanical, or radiation energy. The knowledge of the mechanism of polymer degradation is significant to improve the stability of polymers against decomposition and to characterize polymers by examining their degradation products [3,4]. Decomposition of macromolecules is an important practical topic in polymer science, and is also applicable to basic phenomena in coal or biomass liquefaction, gasification, and combustion. It is fragmentation phenomenon and

fundamental process of great interest in science and engineering.

Most mathematical models developed for investigating the polymer degradation generally consider average properties of the polymer chain-length distribution or molecular-weight distribution (MWD). The population-balance equations are often employed in fragmentation models to describe how frequency distributions of different-size entities, both parent and progeny, evolve. The advantage of these models is that they provide straightforward procedures to derive expressions for monomers of the frequency distributions. The MWD is a partial record of kinetics and its evolution mechanism. Some population models are solved directly from the distribution, but more often the moments are computed and then utilized to construct the distribution as discussed by Laurence et al. [5] and Dotson et al. [6] for polymerization. Population balance equations are written for discrete or continuous MWDs. Continuous kinetics is valid when the MWD allows integrals to represent averages of the distribution. This approach provides governing integro-differential equations that can be directly solved by the moment method.

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Polymer chain scission generally occurs by three steps [7]. The initial step forms radicals. It is followed by depropagation chain reactions (C–C bond cleavage by beta scission) to yield smaller molecular weight (MW) products. The depropagation step is the termination step (by recombination, disproportionation, or hydrogen abstraction) neutralizes radicals. Based on the stationary-state assumption for radical concentrations, one can show that the rate of degradation is first-order in polymer concentration which has been demonstrated experimentally. In many cases, however, polymer chain scission frequently occurs without the second step such as thermal degradation of polyethylene and polypropylene.

The MWD as a function of time (t) can be solved from the batch-reactor population-balance equation and is identical to the steady-state plug-flow reactor result when t is replaced with the residence time. MW moments of the molar MWD provide molar and mass distribution as well as variance and polydispersity of the MWD. Moments provide essential data for the process behavior and are used to construct complete distributions as a function of molecular weight or chain length.

In this work, we describe the degradation behavior of several polymers using the population-model [8–13]. To this aim, several adjustable model parameters are introduced and obtained by fitting experimental data. Each parameter is proven to have different influences on behaviors of MWD for given polymers. The experimental data representing the effect of electron-beam power on the radiolysis of hyaluronic acid are investigated and correlated with the radiation damage to the polymer, as measured in terms of G values.

2. Model descriptions

2.1. Concepts of continuous kinetics for polymer degradation

Polymer degradation can be effectively studied by the continuous-mixture kinetic model. In these models, the polymer is considered to be a mixture with a large number of different-sized molecules, so that MW is a continuous variable. The molar concentration of polymer in the MW range $(x, x + dx)$ is $p(x, t) dx$. Gel-permeation chromatography (GPC) gives the mass MWD, $xp(x, t)$, which can be converted to molar MWD, $p(x, t)$, by dividing by MW, x . MW moments of the molar MWD, $p(x, t)$, are defined by

$$p^{(n)}(t) = \int_0^x x^n p(x, t) dx \quad (1)$$

Thus $p^{(0)}$ is the molar concentration of the polymer (mol/l) and $p^{(1)}$ is the mass concentration (g/l). First and

second moments are determined from experimental measurements of the number and weight-average MWs defined as

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

A continuous mixture undergoes an infinite number of consecutive reactions to yield a wide range of products. The polymer decomposition is considered as a combination of random degradation.

$$A(x') \rightarrow A(x) + A(x' - x)$$

and specific degradation

$$A(x') \rightarrow A(x_i) + A(x' - x_i)$$

where x_i is the molecular weight of a product formed by the specific degradation. The general equation for random degradation is given

$$\frac{dp(x, t)}{dt} = -k(x)p(x, t) + 2 \int_x^\infty k(x')p(x', t)v(x, x') dx' \quad (3)$$

For the specific degradation, two rate equations are required to describe $A(x_i)$ and $A(x' - x_i)$

$$\begin{aligned} \frac{dp(x, t)}{dt} &= -k(x)p(x, t) + \int_x^\infty k(x')p(x', t)v(x - x_i, x') dx' \\ &\text{for } A(x' - x_i) \end{aligned} \quad (4)$$

$$\begin{aligned} \frac{dq(x_i, t)}{dt} &= -k(x)p(x, t) + \int_x^\infty k(x')p(x', t)v(x_i, x') dx' \\ &\text{for } A(x_i) \end{aligned} \quad (5)$$

where $q_i(x, t)$ is the MWD of the product i .

The rate coefficients $k(x)$ are generally dependent on x for both random and specific degradation. We assume that the rate coefficient of the chain scission is independent of MW such as

$$k(x) = k_p x^b \quad (6)$$

where b is a parameter representing the degree of $k(x)$ dependence on molecular weight x . The stoichiometric kernel $v(x, x')$ is defined as

$$\int_0^{x'} v(x, x') dx = 1 \quad (7)$$

and

$$v(x, x') = v(x' - x, x') \quad (8)$$

For polymer degradation, following stoichiometric fraction kernels are employed

$$v(x, x') = B[x(x' - x)]^d: \quad \text{for random degradation} \quad (9)$$

$$\begin{aligned} v(x' - x_i, x') \\ = \delta[x - (x' - x_i)]: \quad \text{for specific degradation} \end{aligned} \quad (10)$$

$$v(x_i, x') = \delta(x - x_i) \quad (11)$$

where B is a constant determined by the normalization condition. MWDs of reactants and products often can be monitored experimentally (e.g., GPC).

The mass of polymer after degradation at time t can be expressed by

$$dp_m/dt = -K(t)(x/M_n) \quad (12)$$

$$K(t) = K_0 \left/ \left(1 + \sum_{j=1} a_j t^j \right) \right. \quad (13)$$

For the decrease of volume of polymer due to degradation,

$$d(V_m p_m)/dt = -K(t) \sum_{j=1} a_j p_m^{(0)} \quad (14)$$

The coefficients, a_j of a polynomial in Eq. (13) is given in Table 1.

2.2. Distribution function

The composition of a product-polymer is usually expressed by a continuous distribution function, $W(I)$, where I is a distribution variable such as a chain length r or a relative molar mass M . In this study, we use the log-normal molar mass distribution function [14].

$$W(I) = \frac{A}{\gamma\sqrt{\pi I}} \exp \left[-\frac{1}{\gamma^2} \left(\ln \frac{I}{I_0} \right)^2 \right] \quad (15)$$

where γ , I_0 , and A are model adjustable parameters. The log-normal distribution has a maximum at I_{MAX} given by

$$I_{MAX} = I_0 \exp(-\gamma^2/4) \quad (16)$$

From this maximum value, we obtain A , which represents the experimental peak height. γ and I_0 are defined by

$$\gamma = \sqrt{2 \ln(\sigma + 1)} \quad (17)$$

$$I_0 = \bar{I}(\sigma + 1)^{1/2} \quad (18)$$

where $\sigma = \mu_2/\bar{I}^2$. μ_2 and \bar{I} are the variance and the average molecular weight of a given sample, respectively.

3. Discussion

3.1. Dependence of the number of scissions on the dose

Since the total number of molecules in a sample before or after chain scission is proportional to [mass of molecule]/[MW of molecule] and scission produces new smaller molecules, so that the reciprocal molecular weight of the polymer provides a line of measure for the number of scissions. Fig. 1 shows the GPC result for the radiolysis of hyaluronic acid [17]. The radiation causes large reductions in the polymer number-average MW with increasing the absorbed dose. Fig. 2 shows the reciprocal of number-average MW plotted against the radiation dose for hyaluronic acid dissolved in water. Results show that the rate of chain scission grows higher with larger amount of electron beam energy absorbed. In other words, the increase of electron-beam energy accelerates the cleavage of polymer chain. In a solution state, the degradation is caused mainly by the free radicals from irradiated water.

3.2. The G value: number of scissions per defined dose

The G value, defined as the number of radiolysis events caused by the absorption of 100 eV of radiation, is the conventional unit to discuss the number of radiolysis events caused by a stated dose [16]. In this study, the events are chain scissions, so the number of scissions attributable to a known dose must be calculated and the

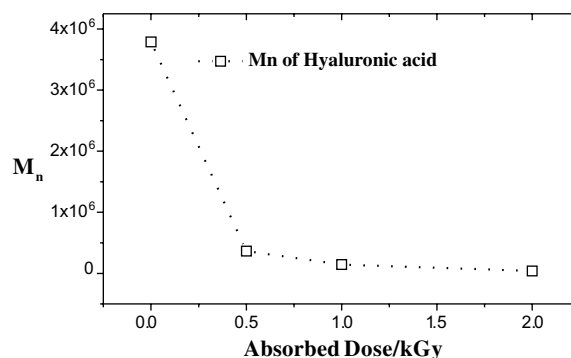


Fig. 1. The extent of decay in MW plotted against gamma dose. The open squares are experimental GPC data.

Table 1
Coefficients for Eq. (12)

T °C	K_0	a_1	a_2	a_3	a_4	a_5	a_6
370	10.1	-0.00711	-0.00037	6.58×10^{-6}	-4.12×10^{-8}	1.16×10^{-10}	-1.14×10^{-13}
390	-115	-0.154	0.00419	4.87×10^{-5}	2.65×10^{-7}	-7.1×10^{-10}	6.81×10^{-13}
400	-20.6	-0.046	0.000832	-7.9×10^{-6}	3.87×10^{-8}	-9.86×10^{-11}	9.2×10^{-14}
410	-12.1	-0.0371	0.000555	-4.51×10^{-6}	1.99×10^{-8}	-4.73×10^{-11}	4.24×10^{-14}

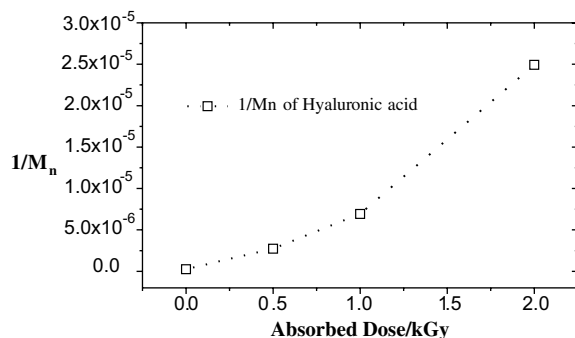


Fig. 2. The plots of the reciprocal MW against gamma dose. The open squares are experimental GPC data.

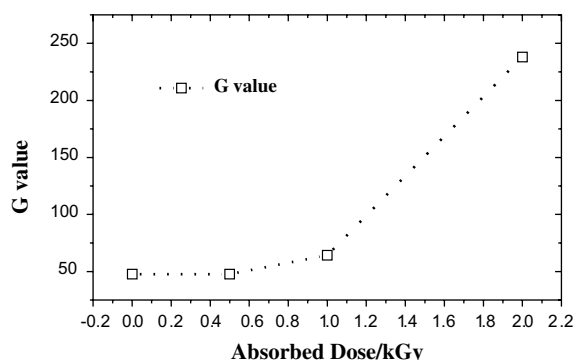


Fig. 3. The G value calculated for the irradiation of hyaluronic acid. The open squares are calculated values using Eq. (16).

result normalized to a dose of 100 eV. The way in which this is done will be evident from the equation below:

$$G = N_A \left[\frac{1}{M_{\text{final}}} - \frac{1}{M_{\text{initial}}} \right] / 6.24 \times 10^{16} D \quad (19)$$

where N_A is the Avogadro's number, D is the dose expressed in kGy, and the term in the bracket denotes the increase in number of molecules due to dose D . Calculated G values for the scission are plotted with respect to dose in Fig. 3. The figure illustrates that the polymer-chain scission occurs more actively with the higher electron-beam energy. This result has a thread of connection with the large decrease of molecular weight in previous one. As shown in this figure, it can be also interpreted that the most of chains are broken scarcely has been irradiated the electron beam.

3.3. MWD's from distribution function

The distribution function employed in this study has three adjustable model parameters; γ , I_0 , and A . Fig. 4

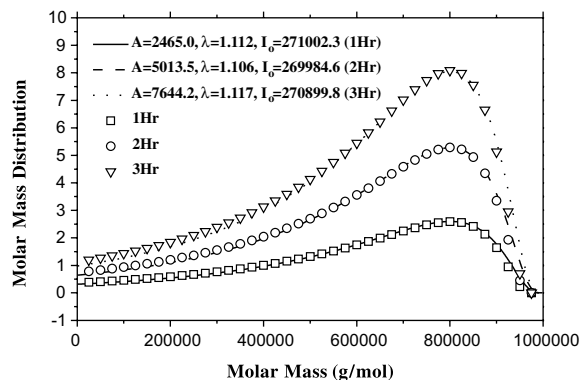


Fig. 4. The effect of pyrolysis time on the MWD of HDPE. The symbols are experimental data reported by Sezgi et al. [15] and the lines are calculated curves from distribution function.

Table 2

Values of model parameters in molar mass distribution function for each pyrolysis time

Parameters	Pyrolysis time		
	1 h	2 h	3 h
γ	1.112	1.106	1.117
I_0	271002.3	269984.6	270899.8
A	2465.0	5013.5	7644.2

indicates the effect of pyrolysis time on the MWD of high-density polyethylene (HDPE). The symbols are experimental GPC data for each pyrolysis time reported by Sezgi et al. [15]. Parameters γ and I_0 are obtained from Eqs. (17) and (18), respectively. Parameter A which represents the experimental peak height is obtained from Eq. (16) ($dW(I_{\text{MAX}})/dI = 0$). Parameter values for each pyrolysis time are listed in Table 2. Experimental GPC results show that the pyrolysis time only influences on the height of maximum peak in the distribution curve.

3.4. Prediction of polymer-melt mass and volume of HDPE

Fig. 5 demonstrates the polymer-melt mass which is plotted against time at four different pyrolysis temperatures; 370, 390, 400, and 410 °C. The symbols are experimental data reported by Sezgi et al. [15], and the lines are calculated from continuous kinetics equation (Eqs. (12) and (13)). Calculated curves show good agreement with the experimental data.

Similar experimental results are given in Fig. 6 compared with calculated values from the continuous kinetics model (Eqs. (13) and (14)). The model again well describes the condition that polymer-melt volume decreases during the reaction progresses.

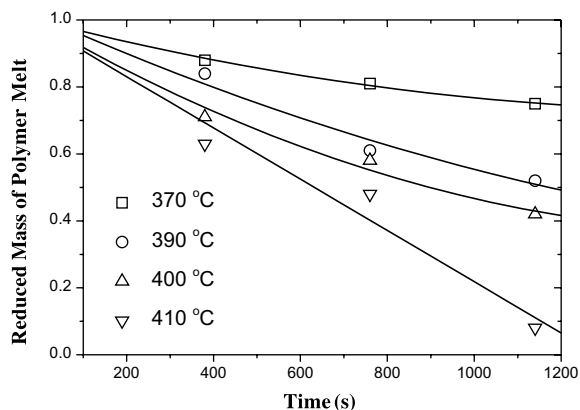


Fig. 5. Change of polymer-melt mass for HDPE with time at four pyrolysis temperatures. The symbols are experimental data reported by Sezgi et al. [15] and the lines are calculated from continuous-kinetics model.

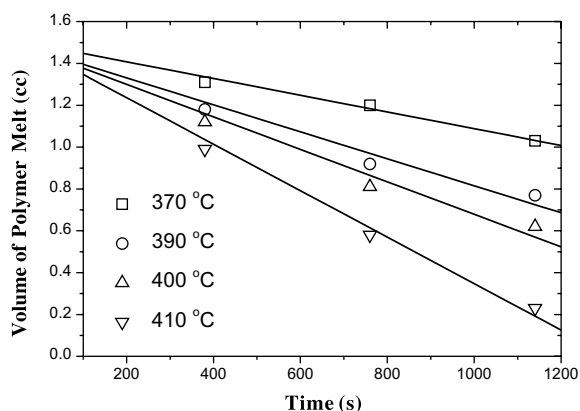


Fig. 6. Change of polymer-melt volume for HDPE with time at four pyrolysis temperatures. The symbols are experimental data reported by Sezgi et al. [15] and the lines are calculated from continuous-kinetics model.

4. Conclusion

In this study, continuous kinetics model is employed to describe degradation behaviors of polymeric liquids. Theory well predicts the decrease of polymer-melt mass and volume of polyethylene according to time at four different pyrolysis temperatures. The MWD of product polymer mixture at three different pyrolysis times is

described by distribution function reported by Chu. Results show that pyrolysis time only influences on the maximum peak of the distribution curve. The MWDs calculated using three adjustable parameters agrees well with the experimental GPC data. The degree of polymer-chain scission can be efficiently represented using G value. From the results of comparison, it is found that the electron-beam energy significantly influences the degradation of hyaluronic acid. In other words, the increase of electron-beam energy causes rapid polymer-chain break, resulting in augmentation of numbers of lower MW molecules.

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