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Effect of hydrogen donors on polymer degradation

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Abstract

The thermal decomposition of hydrocarbon macromolecules, including polymers in solution, is influenced by the presence of hydrogen donors. Depending on the particular polymer, hydrogen donors may increase, decrease, or have no effect on degradation rate. We investigated the concentration effect of the hydrogen- (H-)donor, 6-hydroxy tetralin, on degradation of polystyrene (2 g/l) dissolved in mineral oil at 275°C. The time evolution of the molecular weight distribution (MWD) was determined by gel permeation chromatography of samples from the batch reactor. The data indicated that the H-donor decreases the polystyrene degradation rate. This is in contrast to the H-donor (tetralin) enhancement of degradation for poly(styrene–allyl alcohol) dissolved in a 1-butanol solution at 150°C. Because the reaction mechanism for polymer degradation involves radicals, we have developed continuous-distribution mass balances for polymers and radicals in the elementary reactions by treating molecular weight as a continuous variable. Based on reactions for initiation–termination, propagation–depropagation and H-abstraction, the model describes the various H-donor effects through relative values of rate coefficients. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Polymer degradation; Hydrogen donor; Molecular weight distribution; Thermal decomposition

1. Introduction

Many processes involve thermal decomposition of high molecular weight (MW) compounds to a mixture of low MW products. Thermolysis, pyrolysis, coal liquefaction and hydrocarbon cracking, for example, play important roles in the energy and fuel industries. Understanding the thermal decomposition of macromolecules, which involves bond scission and free-radical propagation, is an important aspect of polymer science and engineering [1]. By pyrolysis, we mean the thermal decomposition of a solid material at high temperatures to yield gas and liquid products of low MW. Thermolysis of polymers in solution produces a mixture of solubilized products. In either case, the decomposition yields a product mixture that often can be described as a continuous function of MW. The time evolution of the molecular weight distribution (MWD) can be examined by continuous-distribution kinetics to determine rate parameters and provide insight into the decomposition mechanisms.

Thermochemical recycling of polymers as either fuel or feedstock has been receiving growing attention in recent years [2]. The research has focused on the mechanism of degradation of pure polymers [3]. The degradation of polystyrene has been extensively investigated by pyrolysis [4] though the mechanism and kinetics of polystyrene degradation remain subjects of

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discussion [5]. Degradation of polymers in solution was proposed to remedy the problems of low heat transfer rates and high viscosity of the melting polymer commonly encountered in polymer recycling by pyrolysis [6]. Investigations have been conducted for degradation in solution of polystyrene [7,8], poly(styrene–allyl alcohol) [9], poly(methyl methacrylate) [10], poly(*p*-methyl styrene) [11] and poly(α-methyl styrene) [12]. The continuous-distribution approach is appropriate for analysis of solubilized polymer degradation kinetics [13] and has also been applied to coal liquefaction [14].

The influence of the solvent is important for degradation of polymers in solution. Sato et al. [6] investigated the solvent effect for polystyrene thermal degradation. Conversion of polystyrene to low MW products decreased with increase of H-donating ability of the solvents. The investigation, however, did not provide values of degradation rate coefficients. Madras et al. [15] found that tetralin enhanced the rate of degradation of poly(styrene–allyl alcohol) and determined rate coefficients as a function of tetralin concentration and temperature. Another study [12] showed that tetralin had no effect on the degradation of poly(α-methyl styrene). Although Kubo [16] emphasized how H-donors can stabilize polymers, published results indicate the varied effect of the H-donor on polymer decomposition. Other experimental studies focused on how H-donor solvents affect the decomposition of hydrocarbons [17], coal [18–20] and model compounds typical of coal [21]. Like polymer degradation, depending on the type of coal and reaction conditions, H-donors increase [22,23] or decrease [24] coal conversion. An overall theory for these observations based on a chemical reaction mechanism is not available.

In the current study, we investigated the effect of H-donors on polymer degradation. In particular, we present new experimental data to show how the H-donor, 6-hydroxy tetralin, influences the degradation rate of polystyrene. A detailed radical mechanism, based on chain reaction concepts, embodies elementary steps of initiation, propagation and depropagation, H-abstraction and termination. Expressions for degradation rate parameters are obtained by applying continuous-distribution kinetics to the MWD of the reacting polymer. The theory explains the different influences of the H-donor solvent on the degradation rate coefficients for different polymers. Though developed for degradation of polymers, the mechanism and the theory are potentially applicable for H-donor effects in other thermal cracking reactions.

2. Experiments

2.1. Analysis of MWDs

The HPLC (Hewlett-Packard 1050) system consists of a 100 μl sample loop, a gradient pump, and an on-line variable wavelength ultraviolet (UV) detector. Three PLgel columns (Polymer Lab) (300 mm× 7.5 mm) packed with cross-linked poly(styrene–divinyl benzene) with pore sizes of 100, 500, and 10^4 Å are used in series. Tetrahydrofuran (HPLC grade, Fisher) was pumped at a constant flow rate of 1.00 ml/min. Narrow MW polystyrene standards of MW 162 to 0.93 million (Polymer Lab and Aldrich) were used to obtain the calibration curve of retention time versus MW.

2.2. Polystyrene degradation

The thermal decomposition of polystyrene in mineral oil was conducted in a 100 ml flask equipped with a reflux condenser to ensure the condensation and retention of volatiles. A volume (60 ml) of mineral oil (Fisher) was heated to 275°C, and various amounts (0–0.60 g) of the H-donor, 6-hydroxy tetralin (Aldrich), and 0.12 g of monodisperse polystyrene (MW= 110 000) (Aldrich) were added. For the non-zero concentrations, the H-donor is always in excess, and therefore its concentration is nearly constant. The temperature of the solution was measured with a Type K thermocouple (Fisher) and controlled within ±3°C using a Thermolyne 45500 power controller. Samples of 1.0 ml were taken at 15 min intervals and dissolved in 1.0 ml of tetrahydrofuran (HPLC grade, Fisher). A 100 μl aliquot of this solution was injected into the HPLC–GPC system to obtain the chromatograph, which was converted to MWD with the calibration curve. Because the mineral oil is UV invisible, its MWD was determined by a refractive index (RI) detector. No change in the MWD of mineral oil was observed when the oil was heated for 3 h at 275°C without polystyrene.

2.3. Theoretical model

Polymers can undergo chain scission to form lower MW products, or undergo addition reactions yielding higher MW products. Chain scission can occur either at the chain end yielding a specific product, or at a random position along the chain yielding a range of lower MW products. Polymers can also react by transforming their structure without change in MW, e.g., by H-abstraction or isomerization. Radicals formed by H-abstraction or chain scission are usually influenced by the presence of the H-donor.

We propose continuous-distribution mass balances for the various steps involved in the radical mechanism. The rate coefficients are independent of MW, a reasonable assumption at low conversions [8]. Integrodifferential equations obtained from the mass balances can be solved in terms of MW moments. In general, moments are governed by coupled ordinary differential equations that can be solved numerically. In the present treatment, two common assumptions allow the equations to be solved analytically. The long-chain approximation (LCA) [25] is valid when initiation and termination events are infrequent compared to H-abstraction and propagation–depropagation events. Thus initiation–termination rates are assumed to be negligible. The quasi-stationary state approximation (QSSA) applies when radical concentrations are extremely small and their rates of change are negligible.

2.4. Case 1: Reversible random-chain scission

Polymer degradation often occurs solely by random-chain scission. The following scheme includes the major elementary steps in the Rice–Herzfeld mechanism [25]. We represent the chemical species of the reacting polymer, and the radicals as $P(x)$ and $R^{\bullet}(x)$ and their MWDs as $p_{\mathrm{tot}}(x,t)$ and $r(x,t)$, respectively, where x represents the continuous variable, MW. Since the polymer reactants and random-scission products are not distinguished in the continuous-distribution model, a single MWD, $p_{\mathrm{tot}}(x,t)$, represents the polymer mixture at any time t. The initiation–termination reactions are represented as

$$P(x) \underset{k_t}{\overset{k_f}{\Leftrightarrow}} R^{\bullet}(x') + R^{\bullet}(x-x') \tag{1.1}$$

where $\Leftrightarrow$ represents a reversible reaction. The reversible H-abstraction process is

$$P(x) + R^{\bullet}(x') \Leftrightarrow P(x') + R^{\bullet}(x) \tag{1.2}$$

In effect, $P(x)$ is converted to a radical, $R^{\bullet}(x)$, and vice versa. For distribution kinetics, this is simply written as

$$P(x) \underset{k_H}{\overset{k_h}{\Leftrightarrow}} R^{\bullet}(x) \tag{1.2a}$$

with pseudo-first-order rate coefficients, k_{h} and k_{H}. The propagation–depropagation reactions are

$$R^{\bullet}(x) \underset{k_a}{\overset{k_b}{\Leftrightarrow}} P(x') + R^{\bullet}(x-x') \tag{1.3}$$

The H-donor reactions are also hydrogen abstractions,

$$P(x) + D^{\bullet} \underset{k_D}{\overset{k_d}{\Leftrightarrow}} R^{\bullet}(x) + D \tag{1.4}$$

where D and $D^{\bullet}$ represent the H-donor and its dehydrogenated form, respectively. The forward reaction produces polymer radicals, while the reverse reaction caps-off (quenches) them. Because the MW of macromolecules $P(x)$ and $R^{\bullet}(x)$ differ only by the atomic weight of hydrogen, we consider they have the same MW, x. We may consider that hydrogenated and dehydrogenated H-donors *both* have the ability to donate or accept hydrogen atoms,

$$P(x) + D \underset{k_D}{\overset{k_d}{\Leftrightarrow}} R^{\bullet}(x) + D^{\bullet} \tag{1.4a}$$

Because D and $D^{\bullet}$ are thus interchangeable, we do not distinguish between their concentrations. As the H-donor, D, is in large excess in our experiments, its concentration, C, is relatively constant. If one assumes that D and $D^{\bullet}$ are in equilibrium through the interchange reaction

$$D \Leftrightarrow D^{\bullet}, \tag{1.5}$$

their concentrations would be related by an equilibrium constant, and rate coefficient values in reactions (1.4) and (1.4a) would be altered by multiplicative constants. Although the rate expressions that result from these assumptions are simplified, we shall show they capture essential behavior and explain observed H-donor effects.

Polystyrene degrades rapidly at low reaction times due to the existence of weak links in the polymer main chain [8,26]. Formed during the addition step of polymerization, weak links are due to the uneven placement of the phenyl groups in the polystyrene main chain. The weak (p_w) and strong (p) links in the polymer (p_{tot}) can be represented by additive distributions,

$$p_{tot}(x,t) = p(x,t) + p_w(x,t). \tag{1.6}$$

Then the molar concentration of the polymer is the sum of molar concentrations of weak and strong links,

$$p^{(0)}_{tot}(t) = p^{(0)}(t) + p^{(0)}_w(t), \tag{1.6a}$$

where $p^{(0)}_{tot}$ is the zero moment. Moments, $p^{(n)}$, are defined as

$$p^{(n)}(t) = \int_0^\infty x^n p(x,t)\,dx. \tag{1.7}$$

The weak link concentration is approximately two orders of magnitude smaller than the strong link concentration [8]. Since weak links have a higher rate of degradation and are depleted within a few minutes, only random rate coefficients of strong links are examined in this study.

The population balance equations for $p(x,t)$ and for radical MWD, $r(x,t)$, are as follows [9,27]:

$$\begin{aligned} dp/dt = {} & -k_f p(x) + k_t \int_0^x r(x')r(x-x')\,dx' - k_h p(x) \\ & + k_H r(x) + k_b \int_x^\infty r(x')\Omega(x,x')\,dx' \\ & - k_a p(x) \int_0^\infty r(x')\,dx' - k_d p(x)C + k_D r(x)C, \end{aligned} \tag{1.8}$$

$$\begin{aligned} dr/dt = {} & 2k_f \int_x^\infty p(x')\Omega(x,x')\,dx' - 2k_t r(x) \int_0^\infty r(x')\,dx' \\ & + k_h p(x) - k_H r(x) - k_b r(x) \\ & + k_b \int_x^\infty r(x')\Omega(x,x')\,dx' \\ & + k_a \int_0^x r(x-x')p(x')\,dx' - k_a r(x) \int_0^\infty p(x')\,dx' \\ & + k_d p(x)C - k_D r(x)C, \end{aligned} \tag{1.9}$$

where $\Omega(x,x')$ is the stoichiometric coefficient (or kernel) [9,13]. Initial conditions are: $p(x,t=0) = p_0(x)$ and $r(x,t=0) = 0$. Applying the moment operation, $\int_0^\infty [\;] x^n\,dx$, yields

$$\begin{aligned} dp^{(n)}/dt = {} & -k_f p^{(n)} + k_t \sum_{j=0}^{n} \binom{n}{j} r^{(j)} r^{(n-j)} - k_h p^{(n)} \\ & + k_H r^{(n)} + k_b Z_{nm} r^{(n)} - k_a p^{(n)} r^{(0)} \\ & - k_d p^{(n)} C + k_D r^{(n)} C, \end{aligned} \tag{1.10}$$

$$\begin{aligned} dr^{(n)}/dt = {} & 2k_f Z_{nm} p^{(n)} - 2k_t r^{(n)} r^{(0)} + k_h p^{(n)} - k_H r^{(n)} \\ & - k_b r^{(n)} + k_b Z_{nm} r^{(n)} + k_a \sum_{j=0}^{n} \binom{n}{j} r^{(j)} p^{(n-j)} \\ & - k_a r^{(n)} p^{(0)} + k_d p^{(n)} C - k_D r^{(n)} C, \end{aligned} \tag{1.11}$$

where [13], $Z_{nm} = \Gamma(2m+2)\Gamma(m+n+1)/[\Gamma(m+1)\Gamma(2m+n+2)]$ and for random scission, m=0.

The initial conditions for moments are

$$p^{(n)}(t=0) = p^{(n)}_0 \quad \text{and} \quad r^{(n)}(t=0) = 0. \tag{1.12}$$

Based on the long-chain approximation, rates of initiation and termination are neglected ($k_f = k_t = 0$). Assuming QSSA, we have

$$dr(x,t)/dt = 0 \tag{1.13}$$

and thus

$$dr^{(n)}/dt = 0. \tag{1.14}$$

For n=0 in Eq. (1.11),

$$r^{(0)} = kp^{(0)}, \tag{1.15}$$

where $k = (k_h + k_d C)/(k_H + k_D C)$ and for n=0, Eq. (1.10) becomes

$$dp^{(0)}/dt = (k_b - k_a p^{(0)}) r^{(0)} = (k_b - k_a p^{(0)}) k p^{(0)}. \tag{1.16}$$

Integrating Eq. (1.16) with the initial condition

$$p^{(0)}(t=0) = p^{(0)}_0 \tag{1.17}$$

yields

$$p^{(0)}(t) = 1/[(k_a/k_b) + \exp(-kk_b t)(1/p^{(0)}_0 - k_a/k_b)]. \tag{1.18}$$

The equilibrium relation is

$$p^{(0)}(t \to \infty) = k_b/k_a. \tag{1.19}$$

For polystyrene degradation experiments [8], lack of evidence of higher MW products indicated the absence of the addition reaction (k_a=0). Thus we have

$$p^{(0)}(t) = p_0^{(0)} \exp(k_r t) \tag{1.20}$$

and a plot of $\ln(p^{(0)}/p_0^{(0)})$ should be linear in time with slope $k_r (= kk_b)$,

$$k_r = k_b(k_h + k_d C)/(k_H + k_D C). \tag{1.21}$$

This is the equation showing how the degradation rate coefficient depends on H-donor concentration. Only zeroth moments (molar concentrations) are required to derive this key relationship, or to determine the rate coefficient k_r from experimental data.

The summation of first moments (n=1) for polymer and radicals (total mass concentration) must be constant when there are no losses from the reactor. For n=1, Eqs. (1.10) and (1.11) are added to obtain

$$\mathrm{d}[r^{(1)} + p^{(1)}]/\mathrm{d}t = 0, \tag{1.22}$$

confirming the mass balance. Applying QSSA,

$$\mathrm{d}r^{(1)}/\mathrm{d}t = 0, \tag{1.23}$$

we have

$$\mathrm{d}p^{(1)}/\mathrm{d}t = 0, \tag{1.24}$$

which is integrated with the initial condition (Eq. (1.12) with n=1),

$$p^{(1)}(t) = p_0^{(1)}. \tag{1.25}$$

The radical mass concentration (Eq. (1.11)) becomes

$$r^{(1)} = (k_h + k_d C + k_a r^{(0)}) p_0^{(1)}/(k_H + k_D C + k_b/2). \tag{1.26}$$

The second moment equations (n=2) are

$$\begin{aligned}\mathrm{d}p^{(2)}/\mathrm{d}t = {} & -(k_h + k_d C)p^{(2)} + (k_H + k_D C)r^{(2)} \\ & + (k_b/3)r^{(2)} - k_a p^{(2)} r^{(0)},\end{aligned} \tag{1.27}$$

$$\begin{aligned}\mathrm{d}r^{(2)}/\mathrm{d}t = {} & (k_h + k_d C)p^{(2)} - (k_H + k_D C)r^{(2)} \\ & - (2k_b/3)r^{(2)} + k_a(p^{(2)} r^{(0)} + 2p^{(1)} r^{(1)}).\end{aligned} \tag{1.28}$$

Since $\mathrm{d}r^{(2)}/\mathrm{d}t = 0$,

$$\mathrm{d}p^{(2)}/\mathrm{d}t = -(k_b/3)r^{(2)} + 2k_a p^{(1)} r^{(1)}. \tag{1.29}$$

From Eq. (1.28),

$$\begin{aligned}r^{(2)} = {} & [(k_h + k_d C + k_a r^{(0)})p^{(2)} + 2k_a p^{(1)} r^{(1)}]/ \\ & (k_H + k_D C + 2k_b/3).\end{aligned} \tag{1.30}$$

Substitution of $p^{(1)}$, $r^{(1)}$, and $r^{(2)}$ in Eq. (1.29) and integration with the initial condition yield

$$\begin{aligned}p^{(2)}(t) = {} & [4k_a(k_b + 3(k_H + k_D C))p_0^{(1)^2}/ \\ & k_b(k_b + 2(k_H + k_D c))] \\ & + [p_0^{(2)} - 4k_a(k_b + 3(k_H + k_D C))p_0^{(1)^2}/ \\ & (k_b(k_b + 2(k_H + k_D C)))] \\ & \times \exp\{k_b[(k_h + k_d C)t \\ & + \log k_b - \log(k_b - k_a p_0^{(0)}(1 - \exp(k_a kt)))]/ \\ & (2k_b + 3(k_H + k_D C))\}.\end{aligned} \tag{1.31}$$

In the absence of addition (k_a=0),

$$p^{(2)}(t) = p_0^{(2)} \exp[-k_b(k_h + k_d C)t/(3(k_H + k_D C) + 2k_b)], \tag{1.32}$$

which is identical to the $p^{(2)}(t)$ expression derived by a simpler model when $2k_b \ll 3(k_H + k_D C)$, i.e.,

$$p^{(2)}(t) \simeq p_0^{(2)} \exp(-k_r t/3). \tag{1.33}$$

The additional term, $2k_b$, is a consequence of the radical mechanism. According to Eq. (1.33), $\ln(p^{(2)}/p_0^{(2)})$ would be linear in time with slope $-k_r/3$, as found by McCoy and Madras [13]. Carrying out the derivation to the second moment, which is a measure of the MWD polydispersity, thus confirms consistency with prior results.

2.5. Case 2: Reversible chain-end scission

Polymers such as poly(α-methyl styrene) undergo degradation by chain-end scission yielding monomers and other low MW specific products, $Q_s(x_s)$. The formation of chain-end radicals by a reversible random-scission initiation/termination reaction is

$$P(x) \underset{k_{ts}}{\overset{k_{fs}}{\Leftrightarrow}} R_e^{\bullet}(x') + R_e^{\bullet}(x - x'). \tag{2.1}$$

H-abstraction by the chain-end radical is considered reversible,

$$P(x) \underset{k_{He}}{\overset{k_{he}}{\Leftrightarrow}} R_e^{\bullet}(x) \tag{2.2}$$

The chain-end radical, $R_e^\bullet(x)$, can also undergo radical isomerization to form a specific radical, $R_s^\bullet(x)$, via a cyclic transition state,

$$R_e^\bullet(x) \overset{k_{ih}}{\underset{k_{iH}}{\Leftrightarrow}} R_s^\bullet(x) \tag{2.3}$$

The reversible propagation–depropagation reaction, whereby a specific radical yields a specific product, $Q(x_s)$, and a chain-end radical, is

$$R_s^\bullet(x) \overset{k_{bs}}{\underset{k_{as}}{\Leftrightarrow}} Q(x_s) + R_e^\bullet(x - x_s) \tag{2.4}$$

The reactions of the H-donor expressed in terms of D, the hydrogenated and $D^\bullet$, the dehydrogenated form of the donor, are

$$P(x) + D^\bullet \overset{k_{de}}{\underset{k_{De}}{\Leftrightarrow}} R_e^\bullet(x) + D \tag{2.4a}$$

The forward reaction is H-abstraction from the polymer; the reverse is H-abstraction from the H-donor. Based on the long-chain approximation, Eq. (2.1) can be neglected. The mechanism represented by Eqs. (2.2)–(2.4) describes the role of the end radical. $Q(x_s)$ represents the specific compound of MW, x_s, formed by chain-end scission of the polymer with strong links, $P(x)$.

The balance equations for $p(x,t)$, $q_s(x,t)$, $r_e(x,t)$, and $r_s(x,t)$ are

$$\mathrm{d}p/\mathrm{d}t = -(k_{he} + k_{de}C)p(x) + (k_{He} + k_{De}C)r_e(x), \tag{2.5}$$

$$\mathrm{d}q_s/\mathrm{d}t = k_{bs}\int_x^\infty r_s(x')\delta(x'-x_s)\,\mathrm{d}x' - k_{as}q_s(x)\int_0^\infty r_e(x')\,\mathrm{d}x', \tag{2.6}$$

$$\begin{aligned}\mathrm{d}r_e/\mathrm{d}t = {} & (k_{he}+k_{de}C)p(x) - (k_{He}+k_{De}C)r_e(x) - k_{ih}r_e(x) \\ & + k_{iH}r_s(x) + k_{bs}\int_x^\infty r_s(x')\delta[x-(x'-x_s)]\,\mathrm{d}x' \\ & - k_{as}r_e(x)\int_0^\infty q_s(x')\,\mathrm{d}x',\end{aligned} \tag{2.7}$$

$$\begin{aligned}\mathrm{d}r_s/\mathrm{d}t = {} & k_{ih}r_e(x) - k_{bs}r_s(x) - k_{iH}r_s(x) \\ & + k_{as}\int_0^x r_e(x'-x_s)q_s(x_s)\,\mathrm{d}x',\end{aligned} \tag{2.8}$$

where the stoichiometric kernels $\delta(\ )$ are defined by Wang et al. [9]. The initial conditions are

$$\begin{aligned}& p(x,t=0) = p_0(x) \quad \text{and} \quad q_s(x,t=0) \\ & \quad = r_e(x,t=0) = r_s(x,t=0) = 0.\end{aligned} \tag{2.9}$$

Applying the moment operation to each balance equation yields

$$\mathrm{d}p^{(n)}/\mathrm{d}t = -(k_{he} + k_{de}C)p^{(n)} + (k_{He} + k_{De}C)r_e^{(n)}, \tag{2.10}$$

$$\mathrm{d}q_s^{(n)}/\mathrm{d}t = k_{bs}x_s^n r_s^{(0)} - k_{as}q_s^{(n)}r_e^{(0)}, \tag{2.11}$$

$$\begin{aligned}\mathrm{d}r_e^{(n)}/\mathrm{d}t = {} & (k_{he}+k_{de}C)p^{(n)} - (k_{He}+k_{De}C)r_e^{(n)} - k_{ih}r_e^{(n)} \\ & + k_{iH}r_s^{(n)} - k_{as}r_e^{(n)}q_s^{(0)} \\ & + k_{bs}\sum_{j=0}^{n}\binom{n}{j}(x_s)^j(-1)^j r_s^{(n-j)},\end{aligned} \tag{2.12}$$

$$\begin{aligned}\mathrm{d}r_s^{(n)}/\mathrm{d}t = {} & k_{ih}r_e^{(n)} - k_{bs}r_s^{(n)} - k_{iH}r_s^{(n)} \\ & + k_{as}\sum_{j=0}^{n}\binom{n}{j}r_e^{(j)}q_s^{(n-j)}.\end{aligned} \tag{2.13}$$

The initial conditions for moments are

$$\begin{aligned}& p^{(n)}(t=0) = p_0^{(n)} \quad \text{and} \quad q_s^{(n)}(t=0) = r_e^{(n)}(t=0) \\ & \quad = r_s^{(n)}(t=0) = 0.\end{aligned} \tag{2.14}$$

Similar to the treatment in random-chain scission, zeroth moments are governed by the following differential equations, where the QSSA for radical species has been applied:

$$\mathrm{d}p^{(0)}/\mathrm{d}t = -(k_{he} + k_{de}C)p^{(0)} + (k_{He} + k_{De}C)r_e^{(0)}, \tag{2.15}$$

$$\mathrm{d}q_s^{(0)}/\mathrm{d}t = k_{bs}r_s^{(0)} - k_{as}q_s^{(0)}r_e^{(0)}, \tag{2.16}$$

$$\begin{aligned}\mathrm{d}r_e^{(0)}/\mathrm{d}t = {} & (k_{he}+k_{de}C)p^{(0)} - (k_{He}+k_{De}C)r_e^{(0)} - k_{ih}r_e^{(0)} \\ & + k_{iH}r_s^{(0)} + k_{bs}r_s^{(0)} - k_{as}r_e^{(0)}q_s^{(0)} = 0,\end{aligned} \tag{2.17}$$

$$\mathrm{d}r_s^{(0)}/\mathrm{d}t = k_{ih}r_e^{(0)} - k_{bs}r_s^{(0)} - k_{iH}r_s^{(0)} + k_{as}r_e^{(0)}q_s^{(0)} = 0. \tag{2.18}$$

Summing Eqs. (2.17) and (2.18) yields

$$r_e^{(0)} = k_e p^{(0)}, \tag{2.19}$$

where $k_e = (k_{he} + k_{de}C)/(k_{He} + k_{De}C)$. Then, Eq. (2.15) is

$$\mathrm{d}p^{(0)}/\mathrm{d}t = 0, \tag{2.20}$$

which can be solved with the initial condition, Eq. (2.14), and the solution is

$$p^{(0)}(t) = p_0^{(0)}. \tag{2.21}$$

This indicates that the molar concentration of polymer is unchanged by chain-end scission. Eq. (2.18) gives

$$r_s^{(0)} = r_e^{(0)}(k_{ih} + k_{as}q_s^{(0)})/(k_{bs} + k_{iH}). \tag{2.22}$$

When the addition reaction is insignificant, then $k_{as} = 0$ and Eq. (2.16) can be solved with Eqs. (2.19) and (2.22),

$$q_s^{(0)}(t) = k_s p_0^{(0)} t, \tag{2.23}$$

where

$$\begin{aligned} k_s = k_e k_{bs} k_{ih}/(k_{bs} + k_{iH}) = (k_{he} + k_{de}C)k_{bs}k_{ih}/ \\ ((k_{bs} + k_{iH})(k_{He} + k_{De}C)). \end{aligned} \tag{2.24}$$

This key result for chain-end scission influenced by H-donor concentration, C, is similar to Eq. (1.21) for random-chain scission. A plot of $q_s^{(0)}(t)/p_0^{(0)}$ versus time would be linear with a slope k_s, which depends on C. This behavior has been experimentally observed for the chain-end scission of poly(styrene–allyl alcohol) [15].

First moment equations for each species are

$$\mathrm{d}p^{(1)}/\mathrm{d}t = -(k_{he} + k_{de}C)p^{(1)} + (k_{He} + k_{De}C)r_e^{(1)}, \tag{2.25}$$

$$\mathrm{d}q_s^{(1)}/\mathrm{d}t = k_{bs}x_s r_s^{(0)} - k_{as}q_s^{(1)}r_e^{(0)}, \tag{2.26}$$

$$\begin{aligned} \mathrm{d}r_e^{(1)}/\mathrm{d}t = {} & (k_{he} + k_{de}C)p^{(1)} - (k_{He} + k_{De}C)r_e^{(1)} \\ & - k_{ih}r_e^{(1)} + k_{bs}(r_s^{(1)} - x_s r_s^{(0)}) - k_{as}r_e^{(1)}q_s^{(0)}, \end{aligned} \tag{2.27}$$

$$\mathrm{d}r_s^{(1)}/\mathrm{d}t = k_{ih}r_e^{(1)} - k_{bs}r_s^{(1)} + k_{as}(r_e^{(1)}q_s^{(0)} + r_e^{(0)}q_s^{(1)}). \tag{2.28}$$

The summation of first moments for polymer and radicals yields

$$\mathrm{d}[p^{(1)} + q_s^{(1)} + r_e^{(1)} + r_s^{(1)}]/\mathrm{d}t = 0. \tag{2.29}$$

Since $\mathrm{d}r_e^{(1)}/\mathrm{d}t = \mathrm{d}r_s^{(1)}/\mathrm{d}t = 0$,

$$\mathrm{d}[p^{(1)} + q_s^{(1)}]/\mathrm{d}t = 0, \tag{2.30}$$

confirming the conservation of polymer mass. It follows that

$$\mathrm{d}p^{(1)}/\mathrm{d}t = -\mathrm{d}q_s^{(1)}/\mathrm{d}t = -x_s\mathrm{d}q_s^{(0)}/\mathrm{d}t. \tag{2.31}$$

When addition does not occur (k_{as}=0), we have

$$q_s^{(1)}(t) = k_s x_s p_0^{(0)} t \tag{2.32}$$

and

$$p^{(1)}(t) = p_0^{(0)}[1 - k_s x_s t]. \tag{2.33}$$

The mass concentration of polymer decreases linearly with time, so that total mass, $q_s^{(1)} + p^{(1)}$, is constant. The time when all polymer disappears to form the specific product, $Q(x_s)$, can also be calculated from the above equation.

The second moment equations are

$$\mathrm{d}p^{(2)}/\mathrm{d}t = -(k_{he} + k_{de}C)p^{(2)} + (k_{He} + k_{De}C)r_e^{(2)}, \tag{2.34}$$

$$\mathrm{d}q_s^{(2)}/\mathrm{d}t = k_{bs}x_s^2 r_s^{(0)} - k_{as}q_s^{(2)}r_e^{(0)}, \tag{2.35}$$

$$\begin{aligned} \mathrm{d}r_e^{(2)}/\mathrm{d}t = {} & (k_{he} + k_{de}C)p^{(2)} - (k_{He} + k_{De}C)r_e^{(2)} \\ & - k_{ih}r_e^{(2)} + k_{iH}r_s^{(2)} + k_{bs}(x_s^2 r_s^{(0)} - 2x_s r_s^{(1)} \\ & + r_s^{(2)}) - k_{as}r_e^{(2)}q_s^{(0)}, \end{aligned} \tag{2.36}$$

$$\begin{aligned} \mathrm{d}r_s^{(2)}/\mathrm{d}t = {} & k_{ih}r_e^{(2)} - k_{iH}r_s^{(2)} - k_{bs}r_s^{(2)} + k_{as}(r_e^{(2)}q_s^{(0)} \\ & + 2r_e^{(1)}q_s^{(1)} + r_e^{(0)}q_s^{(2)}). \end{aligned} \tag{2.37}$$

With k_{as}=0, only degradation occurs, so that

$$q_s^{(2)}(t) = x_s^2 q_s^{(0)} = k_s x_s^2 p_0^{(0)} t \tag{2.38}$$

and

$$\mathrm{d}p^{(2)}/\mathrm{d}t = k_s x_s^2 p_0^{(0)} - 2k_s x_s p^{(1)} + 2k_s^2 x_s p_0^{(0)}/k_{he}, \tag{2.39}$$

$$\begin{aligned} p^{(2)}(t) = {} & p_0^{(2)} + 2x_s^2 p_0^{(0)} k_s t(1 + k_s t) - 2k_s t x_s p_0^{(1)} \\ & + 2k_s^2 t x_s p_0^{(0)}/k_{he}. \end{aligned} \tag{2.40}$$

Eqs. (2.24),(2.32) and (2.38) indicate that specific product moments, $q_s^{(n)}(t)$, increase linearly with time. This is consistent with the equation obtained by a simpler mechanism ignoring the radicals [9] and accurately describes the experimental data [9,12,15].

The equations obtained for polymer moments, Eqs. (2.21),(2.33) and (2.40), are identical to equations derived with the simpler mechanism

[13] if the one term involving k_s^2 is ignored. This negligible term in the second moment is due to inclusion of radicals in the scission mechanism. The new mechanism provides more detailed information on radicals, however, and also provides an explanation for the activation energies observed for random scission and chain-end scission [28].

3. Results and discussion

The rate coefficient for random-chain scission depends on H-donor concentration through elementary-reaction rate parameters k_b, k_h, k_H, k_d, and k_D (Eq. (1.21)). Fig. 1 shows the different effects of the H-donor solvent on the degradation rate coefficient. H-donors can increase, decrease, or have no effect on polymer degradation rate, depending on relative magnitudes of H-abstraction rate coefficients and H-donor concentration. The line for k_r with no approximation was evaluated with k_b=0.001 min^{-1}, k_h=10 min^{-1}, k_H=50 min^{-1}, k_d=k_D=1 l/mol min. To compute other lines in Fig. 1, lesser quantities in the inequalities were set equal to 0. Eq. (2.23) for chain-end scission has the same functional dependence on C as Eq. (1.21) and provides special cases similar to those of Fig. 1.

We determined the random-scission degradation rate coefficient, k_r, from experimental data for polystyrene degradation by analyzing the time dependence of the polystyrene MWDs. Fig. 2 shows $p_{\rm tot}^{(0)}/p_{\rm tot0}^{(0)}$ plotted as a function of time for various 6-hydroxy tetralin concentrations, where $p_{\rm tot0}^{(0)}$ is initial molar concentration of the polystyrene (mol/l) and $p_{\rm tot}^{(0)}$ is molar concentration of polystyrene (mol/l) as a function of time. The plots show a rapid increase in the zeroth moment (corresponding to a rapid decrease of MW) at times less than 45 min. This is attributed to scission of weak links [8,29] randomly distributed along the polymer chain [26].

Fig. 2 and previous experimental data [8] indicate that weak links are totally depleted within 45 min. The initial molar concentration of strong links in polystyrene, $p_0^{(0)}$, is determined from the intercept of the regressed line of the $p_{\rm tot}^{(0)}/p_{\rm tot0}^{(0)}$ data for $t \geq 45$ min. According to Eq. (1.20), slopes corresponding to the random-chain degradation rate coefficient for random scission, k_r , are determined from the plot of $\ln(p^{(0)}/p_0^{(0)})$ versus time (Fig. 3). Fig. 4 shows the rate coefficient decreasing with increasing H-donor (6-hydroxy tetralin) concentration. This negative-

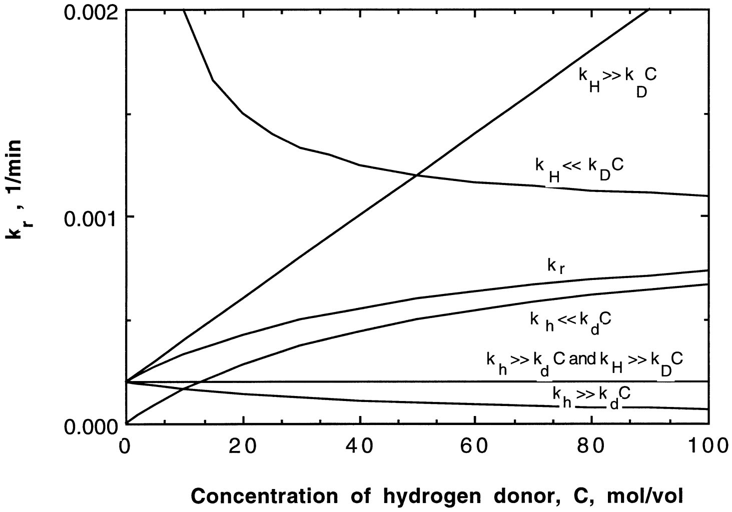

Fig. 1. Plot of the rate coefficient of random-chain scission, k_r, versus H-donor concentration, C (mol/vol), (Eq. (1.21)) to show the different effects of the H-donor concentration and rate parameters.

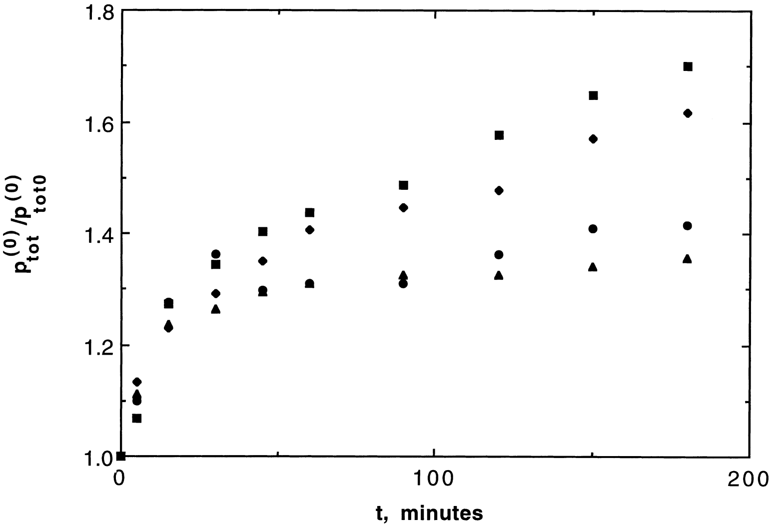

Fig. 2. Plot of $p_{\mathrm{tot}}^{(0)}/p_{\mathrm{tot0}}^{(0)}$ versus time for polystyrene degradation at 275°C for four H-donor (6-hydroxy tetralin) concentrations: (■) polystyrene (2 g/l); (◆) polystyrene (2 g/l)+6-hydroxy tetralin (2 g/l); (●) polystyrene (2 g/l)+6-hydroxy tetralin (5 g/l); and (▲) polystyrene (2 g/l)+6-hydroxy tetralin (10 g/l).

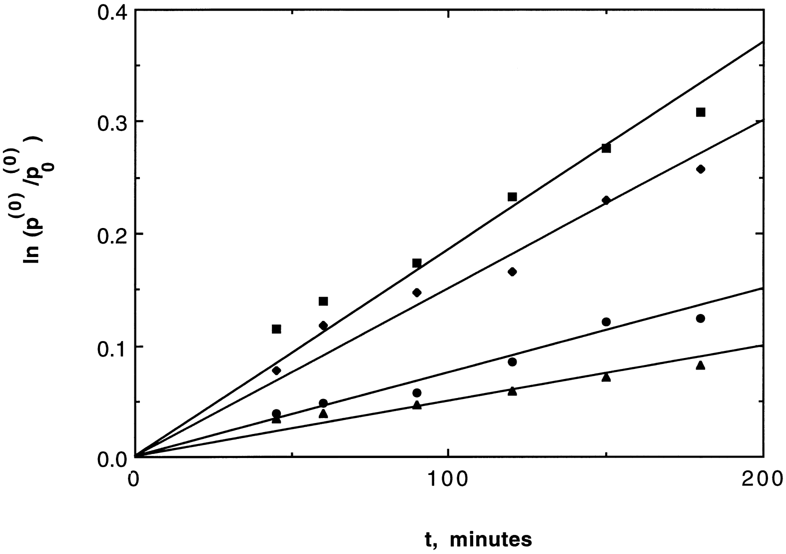

Fig. 3. Plot of $(\ln(p^{(0)}/p_0^{(0)}))$ versus time for polystyrene degradation at 275°C for four H-donor (6-hydroxy tetralin) concentrations, to determine the linearly regressed slopes, k_r (Eq. (1.20)): (■) polystyrene (2 g/l); (◆) polystyrene (2 g/l)+6-hydroxy tetralin (2 g/l); (●) polystyrene (2 g/l)+6-hydroxy tetralin (5 g/l); and (▲) polystyrene (2 g/l)+6-hydroxy tetralin (10 g/l).

order dependence of rate coefficient on H-donor concentration was also observed for polystyrene degradation in presence of tetralin [6]. When $k_h \gg k_d C$, polymer radicals produced by H-abstraction (Eq. (1.2a)) are capped-off (quenched) by H-donor (reverse reaction of Eq. (1.4)). Thus, Eq. (1.21) is $k_r = k_b k_h/(k_H + k_D C)$ and the plot of $1/k_r$ versus molar concentration of 6-hydroxy tetralin (Fig. 4)

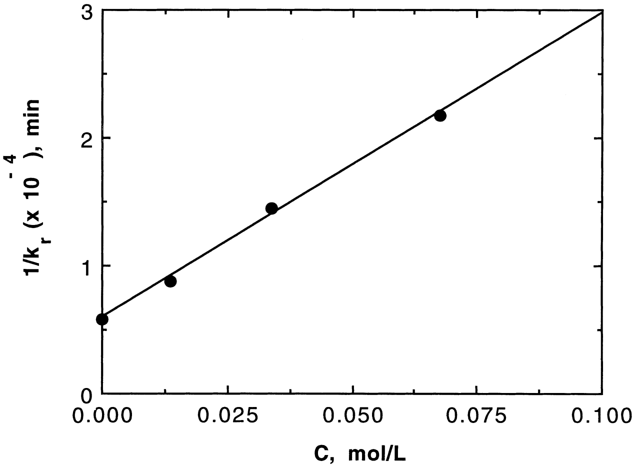

Fig. 4. Effect of H-donor (6-hydroxy tetralin) molar concentration, C, on the rate coefficient of random-chain scission, k_r, of polystyrene at 275°C.

yields ratios of radical rate coefficients from the slope, $k_D/(k_b k_h)$=2.4×10^5 min l/mol, and intercept, $k_H/(k_b k_h)$=5.9×10^3 min. Specific products, styrene and various oligomers, are also produced by chain-end scission of polystyrene. The production rates of these specific products, however, could not be determined because 6-hydroxy tetralin overlapped the monomer and oligomer peaks in the GPC chromatograph.

H-donors sometimes increase the polymer degradation rate. When $k_h \ll k_d C$, polymer radicals are produced primarily by the H-donor (Eq. (1.4)) rather than by H-abstraction (Eq. (1.2a)), and Eq. (1.21) becomes $k_r = k_b k_d C/(k_H + k_D C)$. The rate coefficient has a first-order dependence at low H-donor concentrations and a zero-order dependence at high H-donor concentrations. This behavior was experimentally observed for random-chain poly(styrene–allyl alcohol) degradation in presence of tetralin at 150°C [15]. No degradation occurred in the absence of H-donor (C=0) at investigated temperatures (T<200°C). Ratios of radical rate parameters were obtained from the slope, $k_H/(k_b k_d)$=9.3×10^4 min vol%, and intercept, $k_D/(k_b k_d)$=1.4×10^3 min, of the plot of the inverse of the rate coefficient versus inverse of tetralin concentration (Fig. 5). Fig. 6 shows similar behavior for chain-end scission of poly(styrene–allyl alcohol) to an oligomer of styrene and allyl alcohol (SA) at 150°C [15]. The dependence is consistent with Eq. (2.24) when $k_{he} \ll k_{de} C$, i.e., $k_s = k_{de} k_{bs} k_{ih} C/[(k_{bs} + k_{iH})(k_{He} + k_{De} C)]$. The slope, 7.5×10^3 min vol%, and intercept, 3.2×10^2 min, of Fig. 6 yield ratios of rate parameters.

In certain cases of polymer degradation, H-donors have no effect on degradation rate. When $k_{he} \gg k_{de} C$ and $k_{He} \gg k_{De} C$, the rate coefficient is independent of

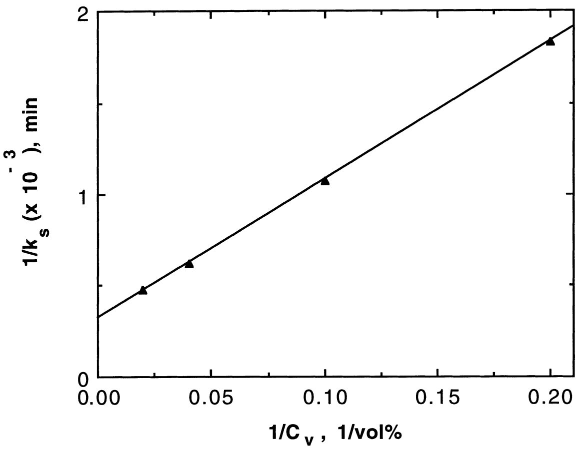

Fig. 5. Effect of H-donor (tetralin) concentration (vol%), C_v, on the rate coefficient of random-chain scission, k_r, of poly(styrene–allyl alcohol) at 150°C.

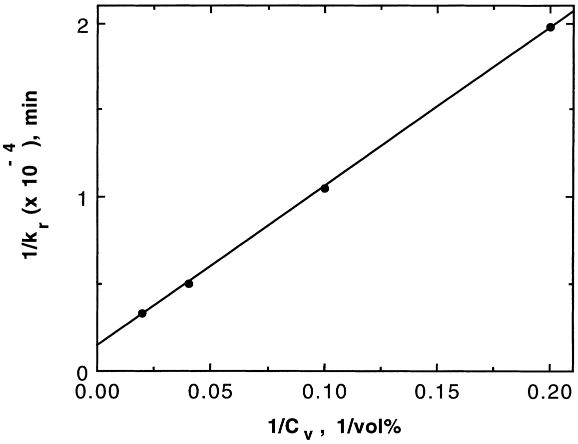

Fig. 6. Effect of H-donor (tetralin) concentration (vol%), C_v, on the rate coefficient of chain-end scission, k_s, of poly(styrene–allyl alcohol) to styrene–allyl alcohol at 150°C.

H-donor concentration because Eq. (2.24) becomes $k_s = k_{he}k_{bs}k_{ih}/[k_{He}(k_{bs}+k_{iH})]$. This is consistent with poly(α-methyl styrene) degradation, which is not affected by H-donor solvents [11,12]. H-donors are unable to abstract hydrogen because the α-position of poly(α-methyl styrene) is blocked by the methyl group.

4. Concluding remarks

A macromolecule undergoing thermolysis typically fragments into smaller chains by random scission and to a lesser extent into oligomers and monomers by chain-end scission. The proposed model for chain scission degradation reactions accounts for radical mechanisms of initiation–termination, H-abstraction, degradation and repolymerization reactions. The theoretical analysis, based on continuous-distribution kinetics of homologous macromolecules, explains the different effects of H-donors on polymer degradation. Depending on the particular polymer, H-donors increase, decrease or have no effect on polymer degradation. Eqs. (1.21) and (2.24) relate random-chain and chain-end scission rate coefficients to H-donor concentration. The dependence of degradation rate on H-donor concentration is determined by relative rates of hydrogen abstraction steps. The radical mechanism provides an explanation for the experimentally observed effects of H-donors on degradation rates.

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