

DISTRIBUTION KINETICS OF DEGRADING POLYMER MIXTURES

Giridhar Madras and Ben J. McCoy
Department of Chemical Engineering and Materials Science
University of California, Davis, CA 95616
email: bjmcocoy@ucdavis.edu

ABSTRACT

Disposal of plastic waste is a worldwide problem that has prompted investigation of plastics recycling, including thermolysis methods. Most basic research on degradation, however, is for single polymers. Waste streams usually contain mixtures of polymers and it may be costly to separate them prior to degradation. Degradation rates depend on the mixture type, and adding another polymer can increase, decrease, or leave unchanged the degradation rate of the first polymer. Determining the decomposition mechanisms for polymer mixtures is of great interest for polymer recycling. In this study, we present techniques to determine the degradation kinetics of solubilized binary polymer mixtures by examining the time evolution of molecular-weight distributions (MWDs). Because the reaction mechanism for polymer degradation involves radicals, we have developed an approach that accounts for the elementary reactions of initiation, termination, hydrogen abstraction, and chain scission. We determined the concentration effect of poly(α -methyl styrene) (PAMS) on the random-chain degradation of polystyrene dissolved in mineral oil at 275 °C in a batch reactor by evaluating the time evolution of the MWDs. Molecular-weight moments yielded expressions for the number- and weight-average MW and degradation rate coefficients. The experimental data indicated that the interaction of mixed radicals with polymer by hydrogen abstraction caused the random-chain scission degradation rate of polystyrene to decrease with increasing PAMS concentration.

INTRODUCTION

The rate of polymer degradation can be modified by the addition of conventional free-radical initiators, oxidizers or hydrogen donors but it might be easier to alter the degradation rate by blending two polymers (Gardner et al., 1993). Degradation studies by pyrolysis of polymer mixtures have reported varied results. For example, some reports indicated a significant interaction between polystyrene and polyethylene (Koo and Kim, 1993; Koo et al., 1991; McCaffrey et al., 1996), while others observed no interaction between these polymers (Roy et al., 1978; Wu et al., 1993). The pyrolytic polystyrene degradation rate was significantly enhanced in the presence of *p*- γ (methyl acrylate) and poly(butyl acrylate) at 430 °C (Gardner et al., 1993). Richards and Salter (1964), on the other hand, observed that the rate of polystyrene degradation decreased with increasing molecular weight (MW) of added PAMS. These reports suggest the need for an analysis of the underlying reaction mechanisms.

Degradation of polymers in solution has been proposed to ameliorate problems encountered in commercial applications (Sato et al., 1990). The degradation of polystyrene (Murakata et al., 1993; Madras et al., 1996c), poly(styrene-allyl alcohol) (Wang et al., 1995), poly(methyl methacrylate) (Madras et al., 1996a), PAMS (Madras et al., 1996b) in solution have been investigated. No studies on the degradation of polymer mixtures in solution, however, have been reported.

EXPERIMENTS

The HPLC (Hewlett-Packard 1050) system consists of a 100 μ L sample loop, a gradient pump, and an on-line variable wavelength ultraviolet (UV) detector. Three PLgel columns (Polymer Lab Inc.) (300 mm x 7.5 mm) packed with cross-linked poly(styrene-divinyl benzene) with pore sizes of 100, 500, and 10,000 Å are used in series. Tetrahydrofuran (HPLC grade, Fisher Chemicals) 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 Chemicals) were used to obtain the calibration curve of retention time versus MW, which was stable during the period of the experiments. The calibration curve, modeled as a second-order polynomial, indicates a higher accuracy in the measurement of lower MW polymers.

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. To observe a significant effect of PAMS on the conversion, polystyrene of high MW was chosen. 60 mL of mineral oil (Fisher Chemicals) was heated to 275 °C, and various amounts (0 - 0.60 g) of monodisperse PAMS (MW = 11,000, Scientific Polymer Products), and 0.12 g of monodisperse polystyrene (MW = 330,000, Aldrich Chemicals) were added. The temperature of the solution was measured with a Type K thermocouple (Fisher Chemicals) and controlled within ± 1 °C by a Omega CN-2042 temperature controller. Samples of 1.0 mL were taken at 15 minute intervals and dissolved in 1.0 mL of tetrahydrofuran (HPLC grade, Fisher Chemicals). The chromatograph obtained by injecting 100 μ L of this solution into the HPLC-GPC system was converted to MWD. The peaks of the reacted polystyrene, PAMS, and the oligomers were distinct, so that moments could be calculated by numerical integration. Because the solvent mineral oil is UV invisible, its MWD was determined with a refractive index (RI)

detector. No change in the MWD of mineral oil was observed when the oil was heated for 3 hours at 275 °C without polystyrene.

THEORETICAL MODEL

According to the Rice-Herzfeld mechanism, polymers can transform without change in MW by hydrogen abstraction. Their radicals can also 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.

In the present treatment, two common assumptions simplify the governing equations. The long-chain approximation (LCA) (Nigam et al., 1994; Gavalas, 1966) postulates that the initiation and termination rates are negligible because such events are infrequent compared to hydrogen abstraction and propagation-depropagation chain reactions. The quasi-stationary state approximation (QSSA) applies when radical concentrations are extremely small and their rates of change are negligible. The proposed scheme, based on the Rice-Herzfeld concept (Nigam et al., 1994) of chain reactions, includes the important elementary steps involving radicals.

The degradation rate of polymer A undergoing random-chain scission is influenced by polymer B undergoing chain-end scission. We represent the reacting polymer A and its radicals as $P_A(x)$ and $R^*(x)$ and their MWDs as $p_A(x,t)$ and $r(x,t)$, respectively, where x represents the continuous variable, MW. As the polymer reactants and random scission products are not distinguished in the distribution kinetics model, a single MWD, $p_A(x,t)$, represents the polymer in the mixture at any time, t . The initiation-termination reactions are represented as



where \rightleftharpoons represents a reversible reaction. The reversible hydrogen abstraction process is



The depropagation chain reaction is



The polymer B, the chain-end radical, the specific radical, and the specific product are represented as $P_B(x)$, $R_c^*(x)$, $R_s^*(x)$, $Q_s(x_s)$, respectively, and their corresponding MWDs as $p_B(x,t)$, $r_c(x,t)$, $r_s(x,t)$ and $q_s(x_s,t)$. The formation of chain-end radicals by a reversible random-scission initiation-termination reaction is



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



The chain-end radical can undergo radical isomerization via a cyclic transition state to form a specific radical,

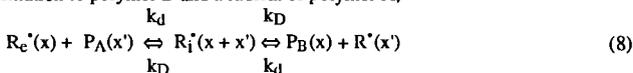


The depropagation reaction yields the specific product and a chain-end radical from a specific radical,



where x_s is the MW of the specific product.

The interaction of the two degrading polymers is through hydrogen abstraction (McCaffrey et al., 1996) represented as a reversible disproportionation reaction. The end radical of polymer B combines with polymer A to form an intermediate radical complex that undergoes transformation to polymer B and a radical of polymer A,



Including the intermediate complex, R_i^* , facilitates the formulation of the population balance equations for the reversible disproportionation. If R_i^* is ignored in equation 1.8, the forward and reverse rate coefficients would be k_d and k_D , respectively.

With the aid of Table 1, the rate expressions and moments can be formulated. Based on LCA, k_f , k_{fs} , k_i and k_{is} are set to zero. The zeroth moments for the polymer, radicals and the monomer, $p^{(0)}$, $r^{(0)}$, $q^{(0)}$ are defined as

$$p^{(0)}(t) = \int_0^\infty p(x,t) dx \quad (9)$$

$$r^{(0)}(t) = \int_0^\infty r(x,t) dx \quad (10)$$

$$q^{(0)}(t) = \int_0^\infty q(x,t) dx \quad (11)$$

The initial conditions for moments are

$$p_B^{(0)}(t=0) = p_{B0}^{(0)}, p_A^{(0)}(t=0) = p_{A0}^{(0)} \text{ and } r^{(0)}(t=0) = 0 \quad (12)$$

When QSSA holds,

$$dr^{(0)}/dt = dr_s^{(0)}/dt = dr_e^{(0)}/dt = dr_i^{(0)}/dt = 0 \quad (13)$$

Algebraic manipulations yield

$$p_A^{(0)}(t) = p_{A0}^{(0)} \exp(k_r t) \quad (14)$$

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

$$k_r = (2 k_b k_H / (k_d p_{B0}^{(0)})) + k_b (k_{bc} + k_b) / k_H \quad (15)$$

The molar concentration is related to the mass concentration, $p^{(1)} = M_n p^{(0)}$, by the average MW, M_n .

The proposed mechanism represents the interaction of radicals of two reacting polymers and shows how the polymer undergoing chain-end scission affects the degradation rate of the polymer undergoing random-chain scission. The degradation rate coefficient is a function of the added polymer concentration, and also depends on the temperature and pressure. This can explain the varied results found in experiments for degradation rates in polymer mixtures.

RESULTS

We have measured the influence of PAMS mass concentration on polystyrene degradation at 275 °C. Because polystyrene degrades by random-chain scission and PAMS degrades by chain-end scission, the polystyrene degradation rate is given by Eqs 14 and 15. The random-scission degradation rate coefficient, k_r , was determined from the experimental data by analyzing the time dependence of the polymer-mixture MWDs. Because the mass of specific products formed by polystyrene chain-end scission at 275 °C for 10 hours is less than 2% (Madras et al., 1996c), we consider that polystyrene degrades solely by random-chain scission.

Polystyrene degrades rapidly at low reaction times due to weak links in the polymer chain caused by side-group asymmetry or chain-branching (Chiantore et al., 1981; Madras et al., 1996c). The weak and strong links in polystyrene can be represented by additive distributions, so that the total molar concentration, $p_{A_{tot}}^{(0)}$, of the polymer is the sum of the molar concentrations of the weak, $p_{A_w}^{(0)}$, and strong links, $p_A^{(0)}$ (Madras et al., 1996c). As the weak link concentration is approximately two orders of magnitude smaller than the strong link concentration, only the random rate coefficients of strong links are examined in this study. The initial molar concentration of the strong links in polystyrene, $p_{A0}^{(0)}$, is determined from the intercept of the regressed line of the $p_{A_{tot}}^{(0)}/p_{A_{tot0}}^{(0)}$ data for $t \geq 45$ minutes (Figure 1). The slopes, corresponding to the rate coefficient for random scission, k_r , are determined from the plot of $\ln(p_A^{(0)}/p_{A0}^{(0)})$ versus time, as given by Eq 14. Madras et al. (1997) show how data are analyzed when the polystyrene degradation rate coefficient is a function of MW, i.e., $k_r(x)$. Equation 15 explains how the polystyrene degradation rate coefficient depends on PAMS concentration. The polystyrene degradation rate coefficient, k_r , decreases with increasing PAMS mass (or molar) concentration. This is consistent with the experimental data (Figure 2 and inset).

The hypothesized interaction of the degrading polymers is through the free radicals and their rates of hydrogen abstraction. When $k_d = k_D = 0$, the two polymers react independently and the moment equations are identical to those derived for a single polymer undergoing chain-end scission or random-chain scission (Madras and McCoy, 1997). The rate coefficient for random-chain scission of polystyrene is a function of the PAMS mixture concentration through the fundamental radical rate parameters, k_b , k_h , k_{bc} , k_d , k_{fi} , and the initial number-average molecular weight of PAMS (Eq 15). The addition of PAMS inhibits the random-chain scission of polystyrene, similar to the effect on hydrogen-donors on the degradation of polystyrene (Madras and McCoy, 1997).

ACKNOWLEDGEMENTS

The financial support of Pittsburgh Energy Technology Center Grant No. DOE DE-FG22-94PC94204 and EPA Grant No. CR 822990-01-0 is gratefully acknowledged.

REFERENCES

Chiantore, O.; Camino, G.; Costa, L.; Grassie, N., "Weak Links in Polystyrene," *Poly. Deg. and Stab.*, **3**, 209 (1981).

Gardner, P.; R. Lehrle; D. Turner, Polymer Degradation Modified by Blending with Polymers Chosen on the Basis of Their Φ -Factors," *J. Anal. Appl. Pyr.*, **25**, 11 (1993).

Gavalas, G. R., "The Long Chain Approximation in Free Radical Reaction Systems," *Chem. Eng. Sci.*, **21**, 133 (1966).

Koo, J.K., S.W. Kim, Y.H. Seo, "Characterization of Aromatic Hydrocarbon Formation From Pyrolysis of Polyethylene-Polystyrene Mixtures," *Resources, Conservation and Recycling*, **5**, 365 (1991).

Koo, J.K., S.W. Kim, "Reaction Kinetic Model for Optimal Pyrolysis of Plastic Waste Mixtures," *Waste Management and Research*, **11**, 515 (1993).

Madras, G., J.M. Smith, B.J. McCoy, "Effect of Tetralin on the Degradation of Polymer in Solution," *I&EC Research*, **34**, 4222 (1995).

Madras, G., J.M. Smith, B.J. McCoy, "Degradation of Poly(Methyl Methacrylate) in Solution," *I&EC Research*, **35**, 1795 (1996a).

Madras, G., J.M. Smith, B.J. McCoy, "Thermal Degradation of Poly(α -Methylstyrene) in Solution," *Poly. Deg. and Stab.*, **52**, 349 (1996b).

Madras, G., J.M. Smith, B.J. McCoy, "Thermal Degradation Kinetics of Polystyrene in Solution," *Poly. Deg. and Stab.*, (1996c); In press.

Madras, G., G.Y. Chung, J.M. Smith, B.J. McCoy, "Molecular Weight Effect on the Dynamics Of Polystyrene Degradation," *I&EC Research*, (1997); In press.

McCaffrey, W.C., Brues, M.J.; Cooper, D.G.; Kamal, M.R., "Thermolysis of Polyethylene Polystyrene Mixtures," *J. App. Poly. Sci.*, **60**, 2133 (1996).

Murakata, T.; Saito, Y.; Yosikawa, T.; Suzuki, T.; Sato, S. "Solvent Effect on Thermal Degradation of Polystyrene and Poly- α -methylstyrene," *Polymer*, **34**, 1436 (1993).

Nigam, A; Fake, D. M; Klein M.T. "Simple Approximate Rate Law for Both Short-Chain and Long Chain Rice Herzfeld Kinetics," *AIChE J.*, **40**, 908 (1994).

Richards, D. H., and Salter, D.A., "Thermal Degradation of Vinyl Polymers I--Thermal Degradation of Polystyrene-Poly(α -methylstyrene) Mixtures," *Polymer*, **8**, 127 (1967).

Roy, M.; Rollin, A.L.; Schreiber, H.P. "Value Recovery from Polymer Wastes by Pyrolysis," *Poly. Eng. Sci.*, **18**, 721 (1978).

Sato, S.; Murakata, T.; Baba, S.; Saito, Y.; Watanabe, S. "Solvent Effect on Thermal Degradation of Polystyrene," *J. Appl. Poly. Sci.*, **40**, 2065 (1990).

Wang, M., J.M. Smith, B.J. McCoy, "Continuous Kinetics for Thermal Degradation of Polymer in Solution," *AIChE J.*, **41**, 1521 (1995).

Wu, C.H.; Chang, C. Y.; Hor, J.L.; Shih, S.M.; Chen, L.W.; Chang, F.W., "On the Thermal Treatment of Plastic Mixture: Pyrolysis Kinetics," *Waste Management*, **13**, 221 (1993).

Table 1. Distribution Kinetics of Primary Reactions.

Stoichiometric kernels: $\Omega(x, x')$ = $1/x'$, $\Omega(x_S, x')$ = $\delta(x - x_S)$, $\Omega(x - x_S, x')$ = $\delta(x - (x' - x_S))$

Reaction Type	Primary Reaction	Rate Expressions	Moment Expressions (k is independent of MW)
Transformation	$R(x) \rightarrow P(x)$	$\partial p/\partial t = -\partial r/\partial t = k r(x, t)$	$dp^{(n)}/dt = -dr^{(n)}/dt = k r^{(n)}(t)$
Random-chain scission	$P(x') \rightarrow Q(x) + R(x' - x)$	$\partial p/\partial t = -k p(x, t)$ $\partial q/\partial t = k \int_x^\infty p(x', t) \Omega(x, x') dx' = \partial r/\partial t$	$dp^{(n)}/dt = -k p^{(n)}(t)$ $dq^{(n)}/dt = k p^{(n)}(t)/(n+1) = dr^{(n)}/dt$
Chain-end scission	$P(x') \rightarrow Q(x_S) + R(x' - x_S)$ x_S is the MW of the specific product	$\partial p/\partial t = -k p(x', t)$ $\partial q/\partial t = k \int_x^\infty p(x', t) \Omega(x_S, x') dx'$ $\partial r/\partial t = k \int_x^\infty p(x', t) \Omega(x - x_S, x') dx'$	$dp^{(n)}/dt = -k p^{(n)}(t)$ $dq^{(n)}/dt = -k x_S^n q^{(0)}(t)$ $dr^{(n)}/dt = k \sum_{j=0}^n \binom{n}{j} x_S^j (-1)^j p^{(n-j)}$
Addition reaction	$P(x') + Q(x - x') \rightarrow R(x)$	$\partial p/\partial t = -k p(x, t) \int_0^\infty q(x', t) dx'$ $\partial q/\partial t = -k q(x, t) \int_0^\infty p(x', t) dx'$ $\partial r/\partial t = k \int_0^x p(x', t) q(x - x', t) dx'$	$dp^{(n)}/dt = -k p^{(n)}(t) q^{(0)}(t)$ $dq^{(n)}/dt = -k q^{(n)}(t) p^{(0)}(t)$ $dr^{(n)}/dt = k \sum_{j=0}^n \binom{n}{j} p^{(j)}(t) q^{(n-j)}$

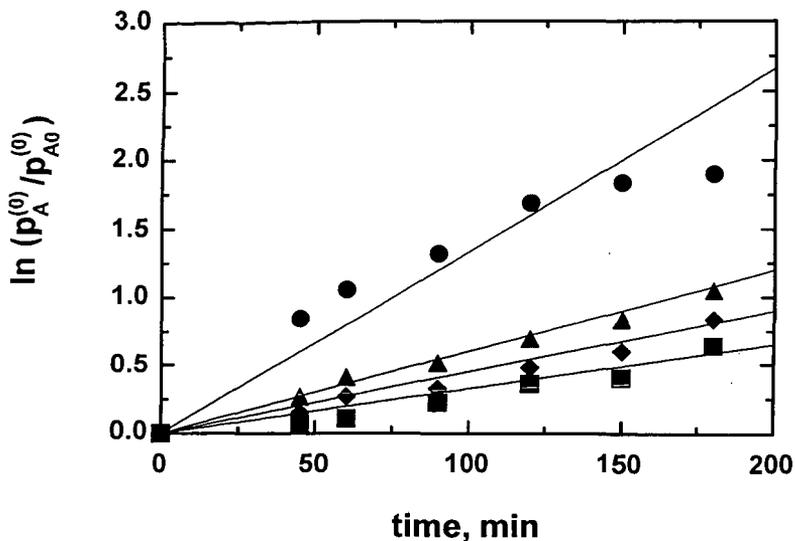


Figure 1. Plot of $\ln(p_A^{(0)}/p_{A0}^{(0)})$ versus time for polystyrene degradation at 275 °C for four PAMS concentrations.
 ● Polystyrene (2/L) only; ▲ Polystyrene (2 g/L) + PAMS (2 g/L); ◆ Polystyrene (2 g/L) + PAMS (5 g/L); ■ Polystyrene (2 g/L) + PAMS (10 g/L).

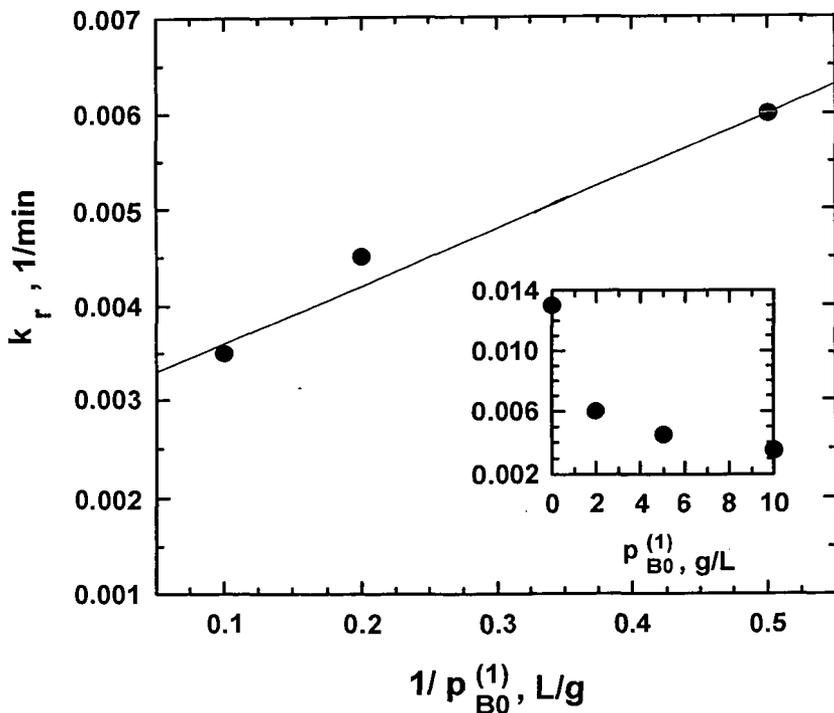


Figure 2. Effect of PAMS mass concentration, $p_{B0}^{(1)}$, on the rate coefficient of random chain scission, k_r , of polystyrene at 275 °C plotted as k_r versus $1/p_{B0}^{(1)}$, as given by equation 1.45. The inset shows k_r versus $p_{B0}^{(1)}$.