

# Effect of Hydrogen Donor on the Thermal Degradation of Poly(vinyl acetate) in Solution

GIRIDHAR MADRAS, SUJAY CHATTOPADHYAY

Department of Chemical Engineering, Indian Institute of Science, Bangalore, 560 012, India

Received 31 July 2000; accepted 18 October 2000

**ABSTRACT:** The thermal decomposition of poly(vinyl acetate) (PVAc) in solution was investigated both in the presence and absence of a hydrogen donor (H-donor). Thermal degradation experiments at 220–250°C were conducted in a batch reactor by dissolving PVAc in diphenylether. The molecular weight distributions were measured as a function of reaction time. Experimental data indicated that the polymer degrades by random chain scission. The random scission degradation rate coefficient was between  $9.01 \times 10^{-4}$  and  $6.12 \times 10^{-3} \text{ min}^{-1}$ . The activation energy, determined from the temperature dependence of the rate coefficient, was 31.5 kcal/mol. The effect of an H-donor, diphenylamine, was also investigated by varying the concentration from 0 to 0.472 mol/L. The data indicated that the presence of diphenylamine increases the PVAc degradation rate from  $3.67 \times 10^{-3}$  to  $4.59 \times 10^{-3} \text{ min}^{-1}$  at 240°C. This is in contrast to the reduction in the degradation rate of polystyrene in the presence of diphenylamine. Continuous distribution models have been developed by treating molecular weight as a continuous variable. The experimentally observed variation of the degradation rates with H-donor concentration is satisfactorily explained by a continuous distribution model based on the radical mechanism that involves the elementary reactions including the hydrogen abstraction steps. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1996–2000, 2001

**Key words:** polymer degradation; polymer solution; continuous distribution kinetics; thermal cracking; hydrogen donor

## INTRODUCTION

Understanding the fundamentals of thermal degradation of polymers is an important aspect of polymer science and engineering.<sup>1</sup> Thermochemical recycling of polymers has been given increasing attention in recent years.<sup>2,3</sup> Though the degradation of polymers has been extensively studied, the mechanism and kinetics of degradation remain subjects of discussion.<sup>4,5</sup> The problems of low heat transfer rates and high viscosity of the

melting polymer<sup>6,7</sup> have hampered the commercial application of polymer recycling by pyrolysis. Degradation in solution has been proposed to ameliorate some of these problems.<sup>6,7</sup> Investigations have been conducted for degradation in solution of polystyrene,<sup>7,8</sup> poly(styrene-allyl alcohol),<sup>9</sup> poly(methyl methacrylate),<sup>10</sup> poly(*p*-methyl styrene),<sup>11</sup> poly( $\alpha$ -methyl styrene),<sup>12</sup> and low density polyethylene.<sup>13</sup>

One of the vital parameters that influence the rate of polymer degradation rate in solution is the hydrogen (H)-donating capability of the solvent. Studies have shown that the presence of H-donor decreases the degradation rate of polystyrene<sup>7,14</sup> and enhances the rate of degradation of poly(styrene-allyl alcohol)<sup>9</sup> but has no effect on the deg-

Correspondence to: G. Madras (giridhar@chemeng.iisc.ernet.in).

*Journal of Applied Polymer Science*, Vol. 81, 1996–2000 (2001)  
© 2001 John Wiley & Sons, Inc.

radiation rate of poly( $\alpha$ -methyl styrene).<sup>12</sup> These studies indicate the varied effect of the H-donor on polymer decomposition. This can be modeled with a continuous distribution model.<sup>14</sup> Several experimental studies<sup>15–18</sup> have also investigated the effect of H-donors on the decomposition of hydrocarbons and coal. Similar to polymer degradation, H-donors increase or decrease coal conversion, depending on the type of coal and reaction conditions. Chiba et al.<sup>15</sup> found that the thermal cracking of bibenzyl, a model compound typical of coal, decreased with increasing H-donating ability of the solvent. Several other studies<sup>16–18</sup> reported improved conversion of coal with the addition of H-donor solvents.

The degradation of polymer yields products that can be described as a continuous function of molecular weight (MW). Continuous distribution kinetics is an effective technique to determine the rate parameters by examining the time evolution of the molecular weight distributions (MWDs). The continuous distribution approach is appropriate for determining the kinetics of polymer degradation and coal liquefaction.<sup>19–22</sup>

The objective of this work was to study the thermal degradation of poly(vinyl acetate) (PVAc) at various temperatures and H-donor concentrations. We present experimental data on how temperature and the presence of H-donor, diphenylamine, increases the degradation rate of PVAc. The experimental data are explained by a detailed radical mechanism that embodies the elementary steps of initiation, depropagation, H-abstraction, and termination. The degradation rate parameters are obtained by applying continuous distribution kinetics to the MWD of the reacting polymer. The activation energy for the random chain scission of PVAc is obtained from the temperature dependence of the rate coefficient.

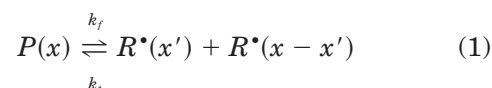
## EXPERIMENTS

The thermal decomposition of PVAc (2 g/L) in diphenyl ether was conducted in a flask (equipped with a long condenser to ensure retention of volatiles) with continuous stirring. The reaction temperature (220–250°C), measured with a thermocouple, was maintained with a controller (Thermotherm). For H-donor experiments, the concentration of diphenylamine was varied between 20–80 g/L at a constant temperature of 240°C. Even though diphenylamine is a poorer H-donor solvent than tetralin,<sup>15</sup> it was chosen as

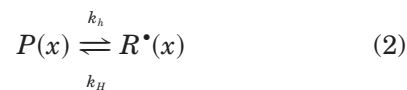
the H-donor solvent because its boiling point (302°C) is much higher than our experimental temperatures. The H-donor concentration is always in excess and, therefore, its concentration is constant throughout the reaction time. Samples of 1.0 mL were taken at regular intervals and 100- $\mu$ L aliquots of these samples were injected into the high pressure liquid chromatograph system. The high pressure liquid chromatograph system (Waters) consists of an isocratic pump, a sample loop, three gel-permeation chromatography columns of varying pore sizes and an online differential refractive index detector. Tetrahydrofuran was used as an eluent and pumped at a constant flow rate of 1.0 mL/min through the system to obtain the chromatograms and converted to MWD with the calibration curve.

## Theoretical Model

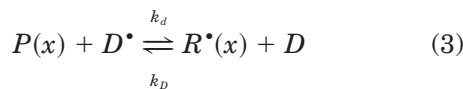
We propose continuous-distribution mass balances for the various steps involved in the radical mechanism.<sup>14,19</sup> These steps include the major elementary steps in the Rice-Herzfeld mechanism,<sup>23</sup> namely, the initiation, termination, H-abstraction,  $\beta$ -scission, and depropagation steps. The reacting polymer and the radicals are represented as  $P(x)$  and  $R(x)$  and their corresponding MWDs are  $p(x,t)$  and  $r(x,t)$ , respectively, where  $x$  represents the continuous variable, MW. Because the polymer reactants and random scission products are not distinguished in the continuous distribution model, a single MWD,  $p(x,t)$ , represents the polymer mixture at any time,  $t$ . The initiation-termination reactions are represented as:



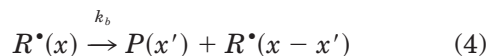
where  $\rightleftharpoons$  represents a reversible reaction. In the reversible H-abstraction process,  $P(x)$  is converted to a radical,  $\dot{R}(x)$  and vice-versa. This is denoted as:



The H-donor reactions are also hydrogen abstractions:



where  $D$  and  $\dot{D}$  represent the H-donor and its dehydrogenated form, respectively. The forward reaction results in increased production of radicals. The reverse reaction caps off (quenches) the radicals formed by reaction 2. We consider the MW of  $P(x)$  and  $R(x)$  the same because they differ only by the atomic weight of hydrogen. The depropagation reaction is:



The population balance equations<sup>9,19</sup> for  $p(x,t)$  and for radical MWD,  $r(x,t)$ , written based on the assumption that the rate coefficients are assumed to be independent of MW, are:

$$\begin{aligned} \partial p / \partial t = & -k_p p(x) + k_t \int_0^x r(x') r(x - x') dx' - k_H p(x) \\ & + k_H r(x) + k_b \int_x^{\infty} r(x') \Omega(x, x') dx' \\ & - k_d p(x) C + k_D r(x) C \quad (5) \end{aligned}$$

$$\begin{aligned} \partial r / \partial t = & 2k_f \int_x^{\infty} p(x') \Omega(x, x') dx' \\ & - k_t r(x) \int_0^{\infty} r(x') dx' + k_H p(x) - k_H r(x) - k_b r(x) \\ & + k_b \int_x^{\infty} r(x') \Omega(x, x') dx' \\ & + k_d p(x) C - k_D r(x) C \quad (6) \end{aligned}$$

The initial conditions are  $p(x,t = 0) = p_0(x)$  and  $r(x,t = 0) = 0$ . The stoichiometric kernel for random scission is  $\Omega(x,x') = 1/x'$ .<sup>9</sup> Applying the moment operation,  $\int_0^{\infty} [ \ ] x'^n dx$ , on eqs. (5) and (6) yields:

$$\begin{aligned} dp^{(n)} / dt = & -k_p p^{(n)} + k_t \sum_{j=0}^n \binom{n}{j} r^{(j)} r^{(n-j)} - k_H p^{(n)} \\ & + k_H r^{(n)} + [k_b r^{(n)} / (n + 1)] - k_d p^{(n)} C + k_D r^{(n)} C \quad (7) \end{aligned}$$

$$\begin{aligned} dr^{(n)} / dt = & [2k_p p^{(n)} / (n + 1)] - 2k_t r^{(n)} r^{(0)} + k_H p^{(n)} \\ & - k_H r^{(n)} - k_b r^{(n)} + [k_b r^{(n)} / (n + 1)] \\ & + k_d p^{(n)} C - k_D r^{(n)} C \quad (8) \end{aligned}$$

The initial conditions for moments are  $p^{(n)}(t = 0) = p_0^{(n)}$  and  $r^{(n)}(t = 0) = 0$ . We assume that the rates of initiation and termination are negligible<sup>23</sup> and that the rates of change of radical concentrations are negligible.<sup>24</sup> The former assumption leads to  $k_f = k_t = 0$  whereas the latter assumption allows us to state  $dr(x,t)/dt = 0$  and thus  $dr^{(n)}/dt = 0$ . For  $n = 0$  in eq. (8):

$$r^{(0)} = (k_h + k_d C) p^{(0)} / (k_H + k_D C) \quad (9)$$

For  $n = 0$ , eq. (7) is:

$$dp^{(0)} / dt = k_r r^{(0)} \quad (10)$$

Integrating eq. (10) with the initial condition,  $p^{(0)}(t = 0) = p_0^{(0)}$ , yields:

$$p^{(0)}(t) = p_0^{(0)} \exp(k_r t) \quad (11)$$

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

$$k_r = k_b(k_h + k_d C) / (k_H + k_D C) \quad (12)$$

Equation (12) depicts the dependence of the degradation rate coefficient on H-donor concentration.

For  $n = 1$ , eqs. (7) and (8) can be added to obtain  $d(r^{(1)} + p^{(1)})/dt = 0$ . Because  $dr^{(1)}/dt = 0$ , we have  $dp^{(1)}/dt = 0$  that can be integrated with the initial condition to yield:

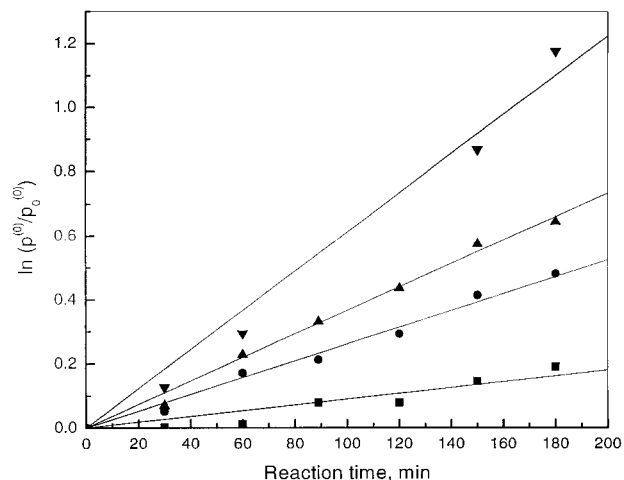
$$p^{(1)}(t) = p_0^{(1)} \quad (13)$$

This confirms the mass balance of the polymer. Equation (11) can be rewritten in terms of the number-average molecular weight,  $M_n$ , defined as  $p^{(1)}/p^{(0)}$  as:

$$M_{n0} = M_n \exp(k_r t) \quad (14)$$

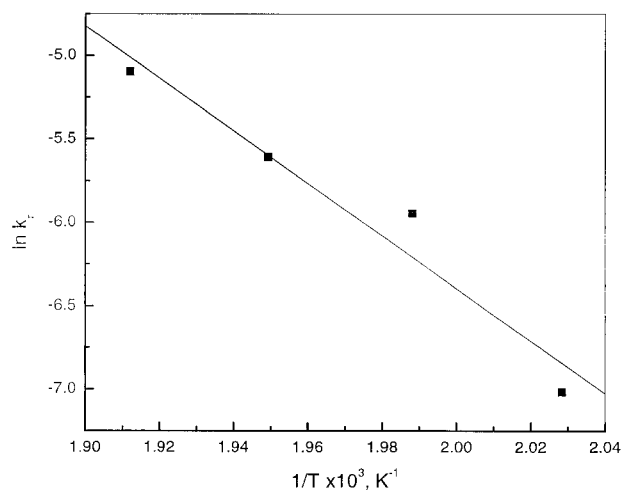
## RESULTS AND DISCUSSION

We determined the random-scission degradation rate coefficient,  $k_r$ , of PVAc from the experimental

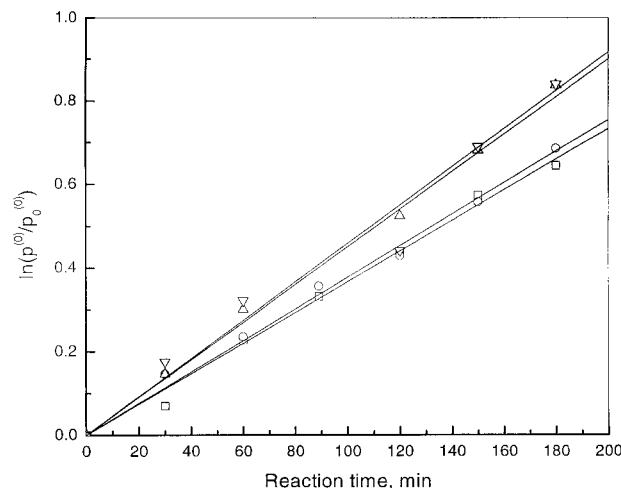


**Figure 1** Plot of  $\ln(p^{(0)}/p_0^{(0)})$  versus time for PVAc degradation at four different temperatures, to determine the linearly regressed slopes,  $k_r$ . ■, 220°C; ●, 230°C; ▲, 240°C; ▼, 250°C.

data by analyzing the time dependence of the MWDs. Figure 1 shows a plot of  $\ln(p^{(0)}/p_0^{(0)})$  versus reaction time for different temperatures.  $p_0^{(0)}$  is the initial molar concentration and  $p^{(0)}$  is the molar concentration of PVAc as a function of time. The plots show a linear trend, as predicted by eq. (11). The slopes, corresponding to the random-chain degradation rate coefficients for random scission,  $k_r$ , are determined from the plot and are  $9.01 \times 10^{-4}$ ,  $2.62 \times 10^{-3}$ ,  $3.67 \times 10^{-3}$ , and  $6.12 \times 10^{-3} \text{ min}^{-1}$  at 220, 230, 240, and 250°C, respectively. Figure 2 shows the Arrhenius plot of the rate coefficient with temperature. The activation



**Figure 2** Arrhenius plot of the random scission rate coefficient,  $k_r$ , of PVAc.



**Figure 3** Plot of  $\ln(p^{(0)}/p_0^{(0)})$  versus time for PVAc degradation at four H-donor concentrations to determine the linearly regressed slopes,  $k_r$ . □, 0 g/L; ○, 20 g/L; △, 40 g/L; ▼, 80 g/L.

energy, determined from the slope of the plot, is 31.5 kcal/mol. This activation energy is comparable to the activation energies reported in the literature for the random chain scission for the thermal degradation of poly(styrene-allyl alcohol)<sup>21</sup> and low density polyethylene in solution.<sup>13</sup>

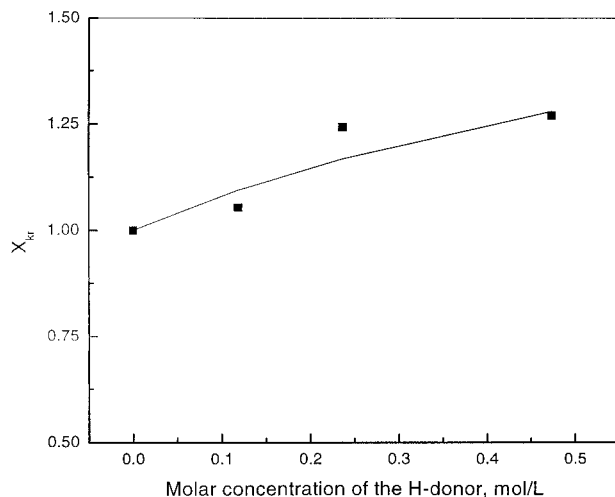
Figure 3 shows the variation of  $\ln(p^{(0)}/p_0^{(0)})$  with reaction time for different concentrations of diphenylamine. The rate coefficients, determined from the slopes, are  $3.78 \times 10^{-3}$ ,  $4.51 \times 10^{-3}$ , and  $4.59 \times 10^{-3} \text{ min}^{-1}$  at 0.118, 0.236, and 0.472 mol/L of diphenylamine concentrations, respectively. This indicates that the rate coefficient increases at low H-donor concentrations but has a zero-order dependence at high H-donor concentrations. Similar behavior has been observed for the thermal degradation of poly(styrene-allyl alcohol) in tetralin.<sup>9</sup> We rewrite eq. (12) as:

$$X_{kr} = k_r/k_{r0} = (1 + (k_d/k_h)C)/(1 + (k_D/k_H)C) \quad (15)$$

and

$$X_{kr} - 1 = ((k_d/k_h) - (k_D/k_H)) C / (1 + (k_D/k_H)C) \quad (15a)$$

where  $k_{r0} = (k_b k_h/k_H)$  is the rate coefficient at zero H-donor concentration. Figure 4 shows a plot of  $X_{kr}$  versus  $C$ , the molar concentration of the H-donor, diphenylamine. Equation (15a) indicates that when  $(k_d/k_h) > (k_D/k_H)$ , the rate of polymer degradation increases with increasing H-



**Figure 4** Effect of H-donor molar concentration,  $C$ , on the rate coefficient of random chain scission,  $k_r$ , of PVAc at 240°C.

donor concentration. The parameters  $k_d/k_h$  and  $k_D/k_H$  are determined from the figure and found to be 2 L/mol and 1.1 L/mol, respectively. Equation (15) can also predict a negative-order dependence of the rate coefficient on the H-donor concentration. When  $(k_d/k_h) < (k_D/k_H)$ , the polymer radicals produced by the H-abstraction reaction are capped off by the hydrogen radical produced by the reverse reaction of eq. (3). The degradation, therefore, decreases with increasing H-donor concentration. This behavior has been observed for polystyrene degradation in the presence of tetralin<sup>6</sup> and diphenylamine.<sup>11</sup> It is apparent, from eq. (15a), that when the ratio of the equilibrium constant of reactions 2,  $K_2 = (k_h/k_H)$  to that of reaction 3,  $K_3 = (k_d/k_D)$ , is less than unity, the degradation increases with increasing H-donor concentration. When the ratio is unity, there is no effect of the H-donor on polymer degradation, as observed for the degradation of poly( $\alpha$ -methyl styrene). Equation (15a) indicates that, for a given polymer, the effect of the H-donor depends not only on the H-donating capability of the donor but also on the stability of the dehydrogenated radical, i.e., on the ratio of  $k_d/k_D$ . A similar conclusion was arrived at by Chiba et al.<sup>15</sup> who observed higher conversions of bibenzyl when the solvents were poor hydrogen donors but their dehydrogenated radicals were more stable. This model,

based on the elementary reactions of polymers, thus accounts for the varied effects of the H-donor on polymer degradation and predicts the increase in the degradation rate of PVAc with H-donor concentration.

## REFERENCES

1. Clough, R. L.; Billingham, N. C.; Gillen, K. T. *Polymer Durability*; ACS Symposium Series, 1996.
2. Miller, A. *Environ Sci Technol* 1994, 28, 16A.
3. McCaffrey, W. C.; Brues, M. J.; Cooper, D. G.; Kamal, M. R. *J Appl Polym Sci* 1996, 60, 2133.
4. Cameron, G. G.; MacCallum, J. R. *J Macromol Sci Rev Macromol Chem* 1967, C1, 327.
5. McNeill, I. C.; Zulfiqar, M.; Kousar, T. *Polym Degrad Stab* 1990, 28, 131.
6. Sato, S.; Murakata, T.; Baba, S.; Saito, Y.; Watanabe, S. J. *J Appl Polym Sci* 1990, 40, 2065.
7. Murakata, T.; Saito, Y.; Yosikawa, T.; Suzuki, T.; Sato, S. *Polymer* 1993, 34, 1436.
8. Madras, G.; Smith, J. M.; McCoy, B. J. *Polym Degrad Stab* 1997, 57, 131.
9. Wang, M.; Smith, J. M.; McCoy, B. J. *AIChE J* 1995, 41, 1521.
10. Madras, G.; Smith, J. M.; McCoy, B. J. *Ind Eng Chem Res* 1996, 35, 1795.
11. Murakata, T.; Wagatsuma, S.; Saito, Y.; Suzuki, T.; Sato, S. *Polymer* 1993, 34, 1431.
12. Madras, G.; Smith, J. M.; McCoy, B. J. *Polym Degrad Stab* 1996, 52, 349.
13. Kumar, S.; Kumar, R.; Madras, G. *J Appl Polym Sci* 2000, to appear.
14. Madras, G.; McCoy, B. J. *Catal Today* 1998, 40, 321.
15. Chiba, K.; Tagaya, H.; Yamauchi, T.; Sato, S. *Ind Eng Chem Res* 1991, 30, 1141.
16. Shishido, M.; Mashiko, T.; Arai, K. *Fuel* 1991, 70, 545.
17. Kershaw, J. R.; Overbeek, J. M. *Fuel* 1984, 63, 1174.
18. Wang, M.; Smith, J. M.; McCoy, B. J. *Energy Fuels* 1993, 7, 78.
19. Kodera, Y.; McCoy, B. J. *AIChE J* 1997, 43, 3205.
20. McCoy, B. J.; Madras, G. *AIChE J* 1997, 43, 802.
21. Madras, G.; Smith, J. M.; McCoy, B. J. *Ind Eng Chem Res* 1995, 34, 4222.
22. Wang, M.; Zhang, C.; Smith, J. M.; McCoy, B. J. *AIChE J* 1994, 40, 131.
23. Nigam, A.; Fake, D. M.; Klein, M. T. *AIChE J* 1994, 40, 908.
24. Chiantore, O.; Camino, G.; Costa, L.; Grassie, N. *Polym Degrad Stab* 1981, 3, 209.