

# Influence of HZSM-5 Catalyst on the Thermal Degradation of Poly(vinyl chloride) in Solution

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**ABSTRACT:** The kinetics of thermal degradation of poly(vinyl chloride) (PVC) in solution was investigated at various temperatures (210–250°C). The degradation rate coefficients were determined from the time evolution of the molecular weight distribution (MWD). The energy of activation, determined from the temperature dependence of the rate coefficient, was 26.6 kcal/mol. The degradation of PVC was also studied in the presence of a catalyst (HZSM-5 zeolite). The results indicated that increase of the degradation rate of PVC is first order with the HZSM-5 concentration up to 50 g/L and zero order at higher concentrations. The thermal degradation kinetics of PVC in the presence of 50 g/L of the catalyst was studied at various temperatures. The temperature dependency of the rate coefficient was used to calculate the activation energy (21.5 kcal/mol). This is consistent with the observation that the presence of a catalyst generally decreases the activation energy and promotes degradation. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 791–796, 2002; DOI 10.1002/app.10332

**Key words:** degradation; GPC; catalysts

## INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most commonly used thermoplastics because of its wide variability of properties allowing its application in rigid or soft products.<sup>1</sup> However, it is not very stable and environmental conditions degrade the polymer quite rapidly. Conventional means of recycling the PVC wastes are pyrolysis, catalytic degradation, melting, and reprocessing of the articles.<sup>2–4</sup> These processes involve the removal of hydrogen chloride (HCl) as one of the products while processing. Considering the en-

vironmental hazards associated with acid removal, these technologies have limited applications.<sup>5</sup>

Patel et al.<sup>6</sup> studied the thermal degradation of PVC in the solid state and showed that hydrochloric acid, removed during the degradation of PVC, acts as an auto catalyst and increases the degradation rate of the PVC. Yassin and Sabaa<sup>7</sup> reviewed the low stability of PVC toward light and heat. Bacaloglu and Fisch<sup>8</sup> inferred that PVC degradation is a complex process and proceeds through a four-center transition state catalyzed by HCl. Li et al.<sup>9</sup> reported that the chain defects in PVC initiates the thermodehydrochlorination with an activation energy of 117.5 kJ/mol. The mechanism of peroxide-induced crosslinking and degradation of PVC was investigated by Yu et al.<sup>10</sup> and chemical initiation followed by thermal initiation was suggested as a probable mechanism. Yoshioka et al.<sup>11</sup> chemically recycled rigid

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PVC by oxidizing with a caustic solution under oxygen pressure at elevated temperatures to obtain raw materials for carboxylic acids. The role of metal oxides in the thermal degradation of PVC was investigated by Gupta and Vishwanath<sup>12</sup> and the formation of metal chloride was reported to be the rate-controlling step. The effect of cadmium chloride<sup>13</sup> and zinc chloride<sup>14</sup> was studied and the activation energy of PVC degradation was reduced with increase of the zinc chloride concentration. Dehydrochlorination of chlorinated hydrocarbon in the liquid phase is accelerated by free HCl or strong electrophilic agents like ZnCl<sub>2</sub> or SnCl<sub>4</sub>.<sup>15</sup> The effect of AlCl<sub>3</sub> in the thermal degradation of PVC was studied by Rogestedt and Hjertberg<sup>16</sup> and it was concluded that an inert atmosphere yields lower dehydrochlorination rates for PVC samples containing AlCl<sub>3</sub> rather than ordinary PVC.

Three main stages of degradation was observed by Chatterjee et al.<sup>17</sup> in the DT–DSC–TG analysis of PVC up to 1000°C in an inert atmosphere. The color change may be attributed to *cis–trans* isomerization, aromatization, and crosslinking.<sup>18</sup> These crosslinked polymers can be further degraded by the HZSM-5 catalyst.<sup>19</sup> Long exposure causes structural degradation of the polymer chains and charring resulting in a brownish reaction mass. A different ionic mechanism may play a role in the degradation with the HZSM-5 zeolite catalyst. Bensemra and Guyot<sup>20</sup> investigated PVC stabilization with and without zinc and calcium stearates and showed that metal stearates reduced the degradation.

Although the effect of catalysts and metals has been extensively studied for the degradation of PVC, as discussed above, the degradation of PVC in solution has not been investigated. Degradation in solution provides several advantages over conventional methods in that there are fewer side reactions and the reaction temperature is lower than for pyrolysis.<sup>21</sup>

In the present work, the thermal degradation of PVC *in solution* was studied both in the presence and in absence of the HZSM-5 zeolite catalyst. The molecular weight distribution (MWD) was obtained from gel permeation chromatography (GPC). A continuous distribution model was used to determine the degradation rate coefficients and the activation energy was determined from the temperature dependence of the rate coefficient.

## EXPERIMENTAL

### Degradation Experiment

A fine powder of PVC (IPCL, India) was used. Commercial-grade diphenyl ether (DPE), obtained from Herdellia Chemicals (Mumbai, India), was twice distilled to obtain a clear liquid. Fifty milliliters of the DPE solution was stirred continuously and increased to the reaction temperature (200–250°C). PVC, 0.1 g, was then added to the reactor. Evolution of HCl was confirmed by testing with a paper soaked in ammonium hydroxide (NH<sub>4</sub>OH). The color change of the reaction mixture initially from colorless to light yellow and finally to brown indicates that reactions occur in three different stages, confirming the mechanism discussed by Chatterjee et al.<sup>17</sup> Samples of 1.0 mL were collected at regular time intervals for analysis by GPC.

### Catalytic Effect of HZSM-5 Zeolite

The HZSM-5 zeolite catalyst (of particle sizes below 0.001 mm) obtained from United Catalyst (Mumbai, India) was used as in various concentrations (2–100 g/L) and at different temperatures (200–250°C). The catalyst was directly added to the reaction mixture.

### GPC Analysis

A 200- $\mu$ l aliquot of the reaction samples was injected into the HPLC–GPC system (Waters Inc). The HPLC consisted of an isocratic pump, a sample loop, three GPC columns (HR4, HR3, HR0.5) of varying pore sizes maintained at 50°C, and an on-line differential refractive index detector. Tetrahydrofuran was used as the eluent and it was pumped at a constant flow rate of 1.0 mL/min. The refractive index is continuously monitored to obtain the chromatograph. The chromatograph is converted to an MWD by the use of a calibration curve, reported in our earlier studies.<sup>22</sup> The initial number-average molecular weight and polydispersity of PVC was 117,000 and 1.37, respectively.

## THEORETICAL MODEL

The overall degradation of polymers can be represented by the following equation:

$$P(x) \rightarrow P(x') + P(x - x') \quad (1)$$

$P(x)$  represents a polymer species of chain length  $x$ , whose molar concentration is represented by  $p(x, t)$ . We assume that the elimination of HCl does not influence the chain length significantly because the molecular weight of the polymer is large. However, this elimination generates the unsaturation at the chain end. Due to absence of any large molecular weight (greater than the initial molecular weight), we assume that no crosslinking or charring occurs. The population balance equation for reaction (1) is<sup>23</sup>

$$\frac{\partial p(x, t)}{\partial t} = -k(x)p(x, t) + 2 \int_0^{\infty} k(x')p(x', t)\Omega(x, x') dx' \quad (2)$$

The stoichiometric kernel,  $\Omega(x, x')$ , represents the fragmentation dynamics and is  $1/x'$  for random breakage of the chain.<sup>23</sup> The degradation rate is assumed to be a linear function of the molecular weight [i.e.,  $k(x) = kx$ ]. Applying the moment operation to eq. (2) yields

$$\frac{dp^{(n)}}{dt} = -kp^{(n+1)} \frac{(n-1)}{(n+1)} \quad (3)$$

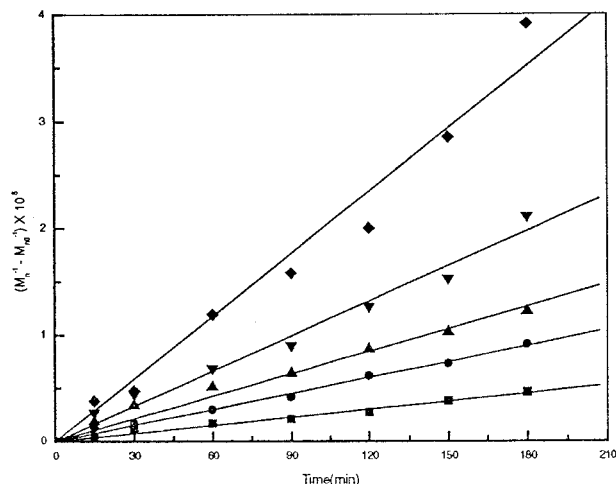
This equation represents the variation of the polymer MWD moments with time. This is solved with the initial condition for the different moments to get the molar concentrations  $p^{(0)}$  and mass concentrations  $p^{(1)}$  of the polymer. These values are then used to find the number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ), and polydispersity ( $P_d = M_w/M_n$ ).

## RESULTS AND DISCUSSION

The zeroth moment ( $n = 0$ ) is

$$\frac{dp^{(0)}}{dt} = kp^{(1)} \quad (4)$$

and is solved with the initial condition,  $p^{(0)}(t = 0) = p_0^{(0)}$ . The first moment ( $n = 1$ ) is  $dp^{(1)}/dt = 0$ , satisfying the conservation of mass of the system, that is,  $p^{(1)} = p_0^{(1)}$ . The solution of eq. (4) is



**Figure 1** Plot of  $M_n^{-1} - M_{n0}^{-1}$  versus time for PVC degradation in DPE at five different temperatures to determine the linearly regressed slopes corresponding to the degradation rate coefficient,  $k$ : (■) 210, (●) 220, (▲) 230, (▼) 240, (◆) 250°C.

$$p^{(0)} - p_0^{(0)} = kp^{(1)}t \quad (5)$$

The above equation reduces to

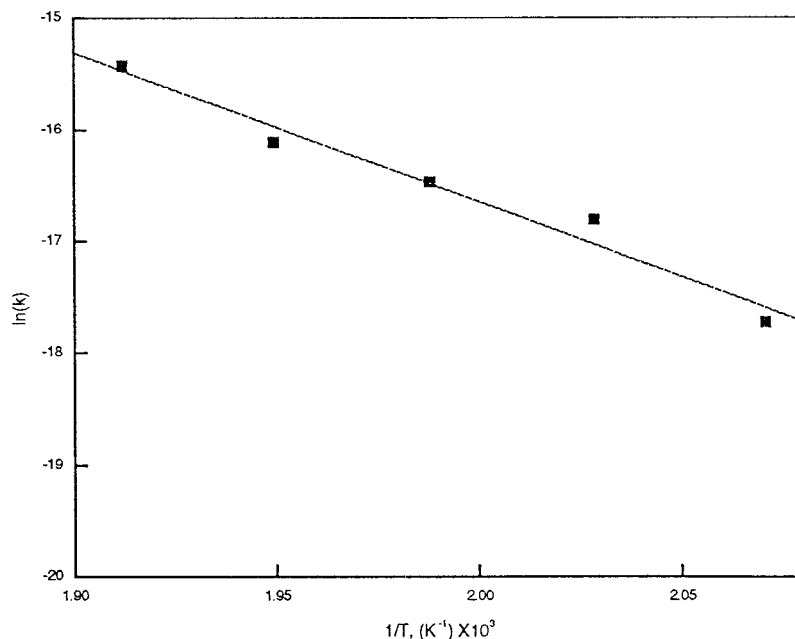
$$(1/M_n) - (1/M_{n0}) = kt \quad (6)$$

in terms of the number-average molecular weight,  $M_n$ , defined as  $p^{(1)}/p^{(0)}$ , indicating that the variation of  $(1/M_n) - (1/M_{n0})$  with time is linear with a slope of the degradation rate coefficient,  $k$ . Figure 1 depicts the time variation of the number-average molecular weight at various temperatures. The slopes give the corresponding degradation rate coefficients. The rate coefficients ( $k \times 10^8$ ) are 2.5, 5.0, 7.0, 11.0, and 19.5 mol g<sup>-1</sup> min<sup>-1</sup> at 210, 220, 230, 240, and 250°C, respectively.

Figure 2 shows the Arrhenius plot of the degradation rate coefficients,  $k$ , of PVC. The energy of activation determined from the slope of Figure 2 is 26.6 kcal/mol. This value is comparable to the pyrolytic dehydrochlorination of PVC (36 kcal/mol)<sup>24</sup> and that observed for the solution degradation of poly(vinyl acetate) (26 kcal/mol).<sup>22</sup>

Figure 3 shows the effect of the HZSM-5 catalyst addition on the degradation rate of PVC. The slopes obtained for different concentrations of HZSM-5 give the rate coefficients at 220°C.

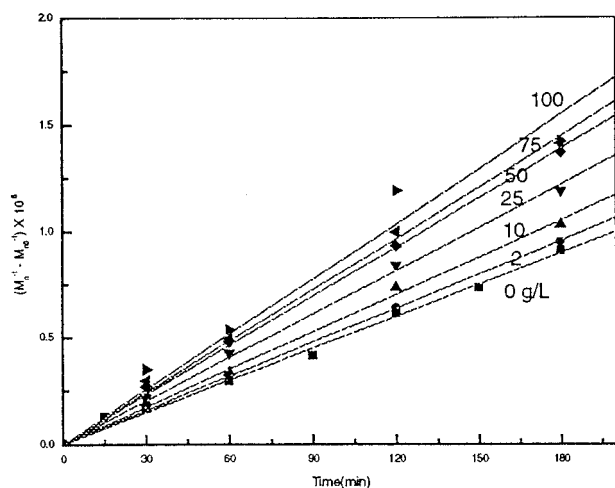
Figure 4 shows that the variation of the degradation rate coefficient with the catalyst concentration. The rate coefficient increases linearly up



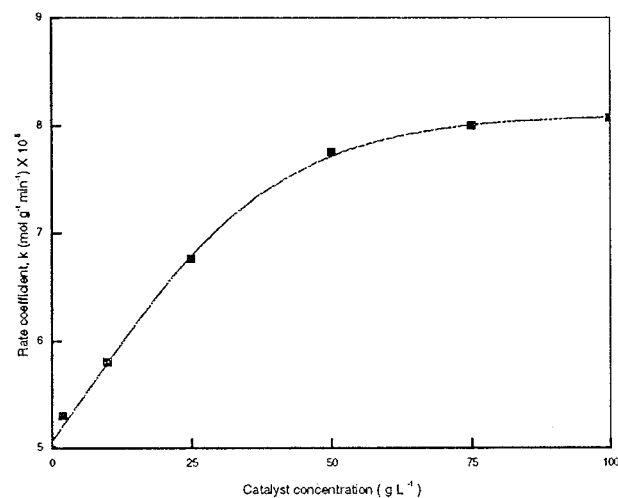
**Figure 2** Arrhenius plot of temperature dependence of the random scission rate coefficient,  $k$ , for PVC in DPE.

to a certain concentration (50 g/L) of HZSM-5 and then the increment in the degradation rate is very small. Thus, the variation of the degradation rate coefficient with the HZSM-5 concentration is first order at low concentrations and zero order at higher concentrations. This enhancement of the degradation rate is in contrast with the investigation of Serrano et al.<sup>19</sup> who observed that an

increasing HZSM-5 concentration reduced the degradation of polystyrene. The reduced degradation was attributed to an ionic mechanism with HZSM-5.<sup>19</sup> A possible explanation for an increase in the degradation rate with increasing HZSM-5 concentration is that the strong Brønsted acid nature of HZSM-5 increases the rate of HCl elimination and, thus, the degradation rate. However, for a given concentration of a polymer, the number of HCl units that can be eliminated from a



**Figure 3** Plot of  $M_n^{-1} - M_{n0}^{-1}$  versus time for PVC degradation in DPE at seven different concentrations (0, 2, 10, 25, 50, 75, and 100 g/L) of HZSM-5 at 220°C. The slopes yield the rate coefficients.

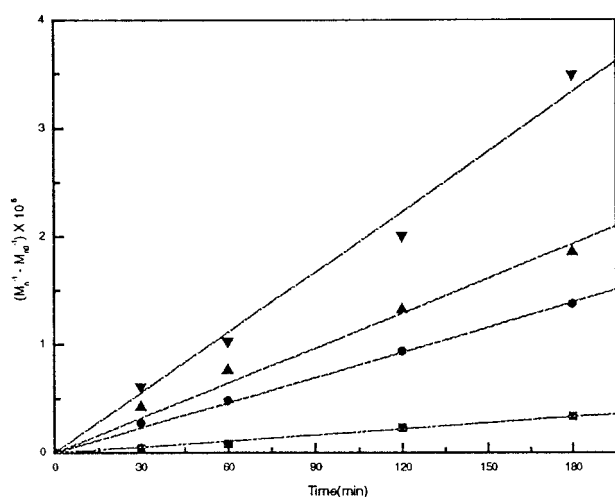


**Figure 4** Variation of the degradation rate coefficients with the mass concentration of HZSM-5.

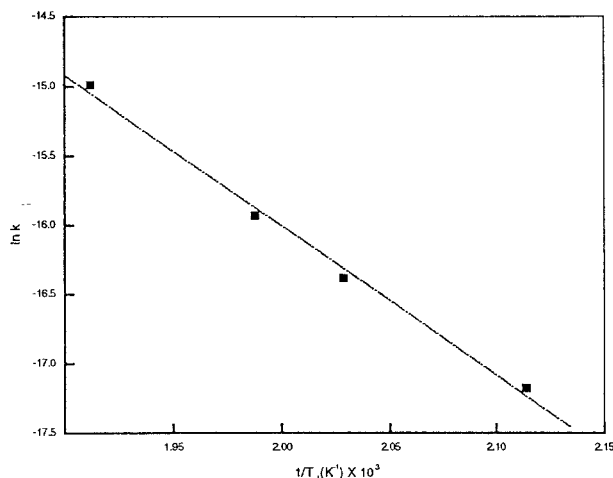
polymer chain cannot increase continuously and, thus, the rate of HCl elimination nearly saturates at a higher catalyst concentration, leading to no significant enhancement of rates at higher concentrations of HZSM-5.

Having determined that the increase of the degradation rate is not significant beyond 50 g/L, this concentration of HZSM-5 was chosen to study the degradation of PVC at 200–250°C. The variation of the number-average molecular weight with time is linear (Fig. 5) and the degradation rate coefficients at various temperatures are obtained from the slopes of the lines. The degradation rate coefficients,  $k$  ( $\times 10^8$ ), of PVC in the presence of the catalyst are 3.5, 7.7, 12, and 31 mol  $g^{-1} min^{-1}$ . It is clear that the degradation rates are enhanced in the presence of the catalyst. For example, the degradation rates at 220°C with and without the catalyst are  $7.7 \times 10^{-8}$  and  $5.0 \times 10^{-8}$  mol  $g^{-1} min^{-1}$ , indicating an increase of the degradation rate of nearly 55% in the presence of the catalyst. The increase in the degradation rate at 250°C is nearly 60%. Figure 6 is the Arrhenius plot of the degradation rate coefficient in the presence of the catalyst and the energy of activation calculated is 21.5 kcal/mol, which is 5.1 kcal/mol lesser than the thermal degradation of PVC in the absence of HZSM-5.

This study thus indicates that the degradation rates of PVC are significantly enhanced in the presence of HZSM-5 at all the investigated temperatures. Although a complex mechanism might



**Figure 5** Plot of  $M_n^{-1} - M_{n0}^{-1}$  versus time for PVC degradation, in DPE in presence of HZSM-5 (50 g/L), at four different temperatures: (■) 200, (●) 220, (▲) 230, and (▼) 250°C.



**Figure 6** Arrhenius plot of temperature dependence of the random scission rate coefficient,  $k$ , for PVC in DPE in presence of HZSM-5.

be involved in the degradation process, the presence of HZSM-5 significantly increases the degradation rate and reduces the activation energy required for degradation.

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