Effect of Aluminum Chloride and Pt/ TiO$_2$ on the Thermal Degradation of Poly(vinyl chloride) in Solution

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ABSTRACT: The effect of two catalysts, Pt/TiO$_2$ and aluminum chloride, on the degradation of poly (vinyl chloride) (PVC) in solution was investigated at various temperatures. The molecular weight distribution of the polymer was obtained by analyzing the samples by gel permeation chromatography. Experimental data indicated that the catalysts enhanced the degradation rate of PVC compared to the thermal degradation of PVC. Continuous distribution kinetic models were used to evaluate the degradation rate coefficients. The activation energy, calculated from the temperature dependence of rate coefficients, was 26.5, 31.5, and 43.7 kcal/mol for the thermal degradation of PVC in solution, in the presence of Pt/TiO$_2$ and in the presence of AlCl$_3$, respectively. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3532–3535, 2003

Key words: degradation; gel permeation chromatography (GPC); kinetics (polym.); catalysts; poly(vinyl chloride) (PVC)

INTRODUCTION

Polyvinyl chloride (PVC) is an important thermoplastic with a wide variety of applications. Understanding the degradation kinetics of the polymer is useful to determine the potential of recycling this polymer safely.

Many studies[1–4] have been reported on the degradation of PVC by pyrolysis. It is observed that the hydrochloric acid liberated during the reaction catalyzes the rate of degradation.[3,4] Metal chlorides have also been found to increase the rate of degradation. The role of metal oxide in the thermal degradation of PVC has been investigated[5] and the formation of metal chloride was reported to be a rate-determining step. It has been reported that thermal treatment of PVC in the presence of AlCl$_3$ at 200°C gave complete dehydrochlorinated mass.[6] However, another investigation[7] reported that PVC containing 0.05 to 4% AlCl$_3$ in nitrogen exhibited lower degradation than the degradation observed during the pyrolysis of PVC.

Despite the large number of studies on the catalytic degradation of polymers in pyrolysis, the catalytic degradation of polymers in solution has not been investigated in detail. The effect of zeolite, HZSM-5, on the degradation of PVC in solution has been investigated recently.[8] The enhancement in the degradation rate of poly(vinyl) acetate[9] and polystyrene[10] in solution in the presence of AlCl$_3$ has also been reported.

In the present work, the thermal degradation of PVC in solution was studied both in the presence of Pt/TiO$_2$ and AlCl$_3$. The degraded samples were analyzed by gel permeation chromatography (GPC) to obtain the molecular weight distribution (MWD). Continuous distribution models were used to determine the degradation rate coefficients, and the activation energies were determined from the temperature dependence of the rate coefficient.

EXPERIMENTAL

Degradation experiments

Diphenyl ether (DPE, S.D. Fine Chemicals, India) was distilled and filtered to obtain a clear liquid. Fifty milliliters of DPE were taken in a round-bottom flask equipped with a reflux condenser to ensure condensation and retention of volatiles. The temperature of the system was increased to reaction temperature (220–250°C) with continuous stirring; 0.25 g of PVC (IPCL, India) was then added to the reactor. 0.05 g (1 g/L) of Pt/TiO$_2$ was added to the reactor just after the addition of PVC. In separate experiments, a weighted amount of AlCl$_3$ (Merck, India) (stored in a dessicator to avoid any moisture absorption) was added to the reactor just after the addition of PVC to study the effect of AlCl$_3$. The Pt/TiO2 catalyst was prepared by the solution combustion technique. The details of the preparation and characterization are provided elsewhere.[11] Experiments were also conducted in the ab-

sence of a catalyst to determine the thermal degradation rate. Several experiments were repeated, and the standard deviation in the molecular weights was less than 2%. Samples of 1.0 mL were taken at regular time intervals for subsequent analysis by GPC.

GPC analysis

A 200-μL aliquot of the reaction sample was injected in the HPLC-GPC system (Waters Inc). The HPLC consist of an isocratic pump, a sample loop, three GPC columns (Styragel HR 4, HR 3, HR 0.5) of varying pore sizes maintained at 50°C and an on-line differential refractive index detector. A data acquisition system was used to obtain a chromatograph and converted to the molecular weight distribution (MWD) using a calibration curve based on polystyrene standards. The initial number average molecular weight of PVC was 110,000 with polydispersity 1.5.

Theoretical models

In developing the continuous distribution models, it is important to recognize the differences between AlCl$_3$ and Pt/TiO$_2$ in catalyzing the degradation of PVC in solution. Pt/TiO$_2$ does not decompose during the reaction, and retains its activity for several experiments. In contrast, AlCl$_3$ decomposes during the reaction and loses its activity. Thus, two different models are developed to model the reactions.

Thermal degradation and effect of Pt/TiO$_2$

The overall degradation reaction of polymer can be represented by the equation:

$$P(x) \rightarrow P(x') + P(x - x') \tag{1}$$
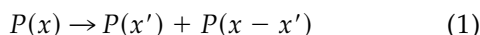
where $P(x)$ represents a polymer species of length x, whose molar concentration is given by $p(x,t)$. It is assumed that the elimination of HCl does not influence the chain length significantly because the molecular weight of the polymer is large. However, this elimination generates the unsaturation at the chain end, which leads to further degradation of the polymer. It was also observed that no crosslinking or charring occurs during the reaction. The population balance equation for the reaction is[12]

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

The stoichiometric kernel, ω (x,x'), represents the fragmentation dynamics and is $1/x'$ for random

breakage of the chain.[12] The degradation rate coefficient is assumed to be a linear function[8,12,13] of molecular weight, $k(x) = k\ x$. Applying the moment operation,

$$p^{(n)}(t) = \int_{0}^{\infty} x^n p(x,t)dx \tag{3}$$

Equation (2) reduces to

$$\frac{dp^{(n)}}{dt} = -kp^{(n+1)}\frac{(n-1)}{(n+1)} \tag{4}$$

Equation (4) represents the variation of the polymer MWD moments with time.

Effect of AlCl$_3$

When AlCl$_3$ catalyzes the reaction, it dissociates and is consumed during the reaction. Thus, the effect of AlCl$_3$ decreases with reaction time and, at longer reaction time, AlCl$_3$ does not play a role in the reaction. The overall reaction can be represented by

$$P(x) + C \rightarrow P(x') + P(x - x') + C' \tag{5}$$
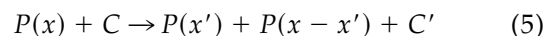
The population balance equation for the reaction is written as

$$\frac{\partial p(x,t)}{\partial t} = -k_t(x)p(x,t) + 2\int_{x'}^{\infty} k_t(x')p(x',t)\Omega(x,x')dx'$$
$$+ -k_c(x)p(x,t)c(t) + 2\int_{x'}^{\infty} k_c(x')p(x',t)\Omega(x,x')c(t)dx' \tag{6}$$

The rate coefficients in eq. (6), k_c and k_t, represent the thermal degradation of PVC in the presence and absence of AlCl$_3$, respectively. The stoichiometric kernel, ω (x,x'), is $1/x'$ for random breakage of the chain.[12] The rate coefficients can be assumed to depend linearly on the molecular weight of the polymer[8,12,13] and, thus, $k_c(x) = k_c\ x$ and $k_t(x) = k_t\ x$. The equation for change in concentration of AlCl$_3$ can be written as
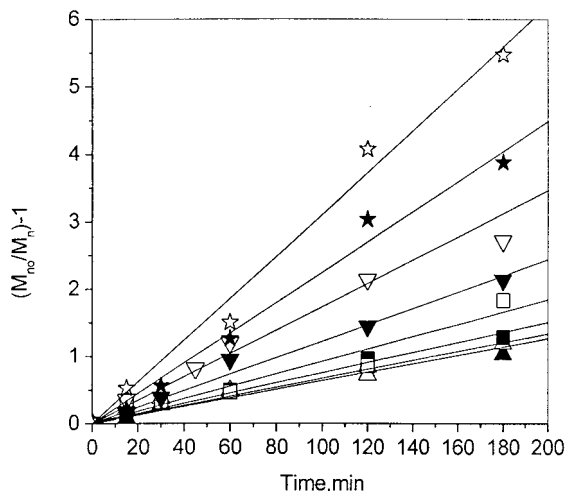
Figure 1 Degradation of PVC in the absence (solid symbols) and in the presence of Pt/TiO$_2$ (hollow symbols) at various temperatures. Legends: (★: 250°C; ▼: 240°C; ■: 230°C; ▲: 225°C.

$$\frac{\partial c}{\partial t} = -k_a c(t) - \int_0^\infty k_c(x')p(x',t)c(t)dx' \qquad (7)$$

The rate coefficient, k_a, represents the dissociation of AlCl$_3$ and is independent of the molecular weight of the polymer. Substituting the expressions for the rate coefficients and applying the moment operation on eqs. (6) and (7) yields,

$$\frac{dp^{(n)}}{dt} = -(c(t)k_c + k_t)p^{(n+1)}\frac{(n-1)}{(n+1)} \qquad (8)$$

$$\frac{dc}{dt} = -k_a c(t) - k_c c(t)p^{(1)} \qquad (9)$$

RESULTS AND DISCUSSION

The approach has been to derive the moments of the polymer MWD, represented by eqs. (4) and (9), for the two different degradation process. The variation of the zeroth and first moments with time can be directly obtained by substituting $n = 0$ and 1 in these equations. These values are then used to find the number-average molecular weight (M_n), defined as the ratio of the first moment to the zeroth moment. The variation of the first moment is $dp^{(1)}/dt = 0$, indicating that the $p^{(1)} = p_o^{(1)}$, satisfying the mass conservation.

Thermal and effect of Pt/TiO$_2$

The thermal and Pt/TiO$_2$ catalyzed degradation of PVC was investigated at various temperatures. The

zeroth moment, obtained from eq. (4) with $n = 0$, is $dp^{(0)}/dt = kp^{(1)}$ and solved with the initial condition $p_{(0)}(t=0)=p_o^{(0)}$ to obtain $p^{(0)} - p_o^{(0)} = kp_0^{(1)}t$. This can be written in terms of the number-average molecular weight M_n, defined as $p^{(1)}/p^{(0)}$,

$$\frac{M_{no}}{M_n} - 1 = M_{no}kt \qquad (10)$$

Figure 1 shows the variation of (M_{no}/M_n-1) with time for the noncatalytic thermal degradation and Pt/TiO$_2$ catalyzed degradation of PVC. The variation is linear, as suggested by eq. (10). The degradation rate coefficients ($\times 10^8$ mol g^{-1} min^{-1}), obtained from the linearly regressed slopes, are 5.7, 6.8, 11.1, and 20.5 for the noncatalytic thermal degradation of PVC and 6.1, 8.4, 14.8, and 28.2 at 225, 230, 240, and 250°C for the Pt/TiO$_2$ catalyzed degradation of PVC, respectively. This shows a 6.4% increase in degradation rate at 225°C and 27.4% at 250°C, indicating that Pt/TiO$_2$ enhances the rates better at higher temperatures.

Figure 2 shows the Arrhenius plot of the degradation rate coefficients. The activation energies, obtained from the regressed lines, are 26.5 and 31.5 kcal/mol for the thermal and catalytic degradation of PVC, respectively.

Effect of AlCl$_3$

The degradation of PVC in presence of AlCl$_3$ was investigated at various temperatures. The zeroth moment, obtained from eq. (9) with $n = 0$, is
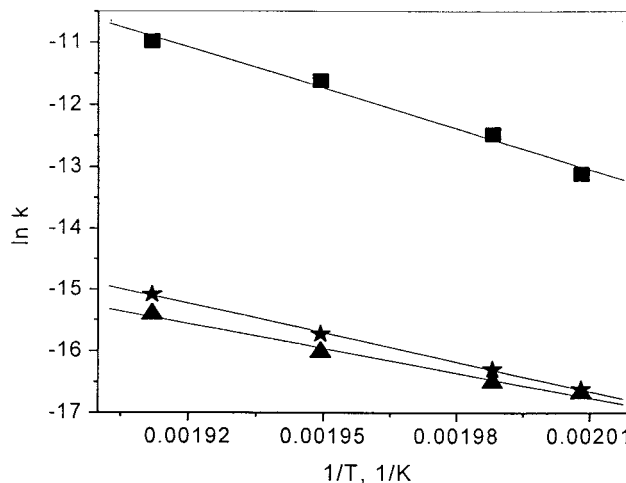

Figure 2 Arrhenius plot of rate coefficients with temperature to determine the activation energy for the degradation of PVC. ▲: Thermal degradation rate coefficient, k_t, without catalyst; ★: thermal degradation rate coefficient, k, in the presence of Pt/TiO$_2$; ■: thermal degradation rate coefficient, k_c, in the presence of AlCl$_3$.
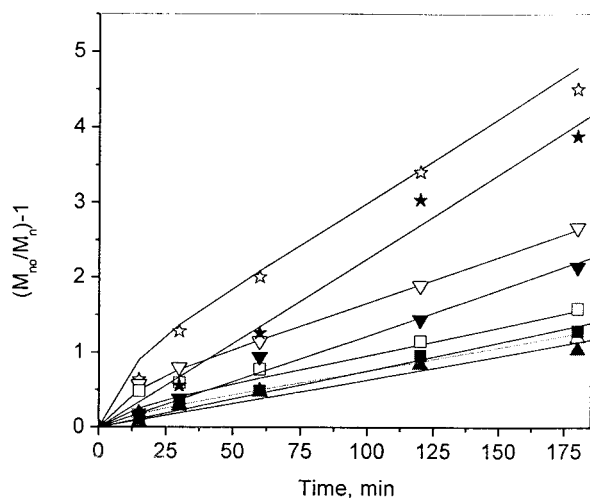
Figure 3 Degradation of PVC in the absence (solid symbols) and in the presence of AlCl$_3$ (hollow symbols) at various temperatures. See Figure 1 for legend.

$$\frac{dp^{(0)}}{dt} = k_t p^{(1)} + k_c p^{(1)} c(t) \tag{11}$$

Equation (11) is solved by first solving eq. (8) and substituting the expression for $c(t)$ in eq. (11). The solution for eq. (11) is

$$\frac{M_{no}}{M_n} - 1 = k_t M_{no} t + \frac{k_c M_{no} c_0}{(k_a + k_c p^{(1)})}$$
$$\times (1 - \exp(-(k_a + k_c p^{(1)})t)) \tag{12}$$

Equation (12) indicates that the variation of $(M_{no}/M_n - 1)$ with time AlCl$_3$ catalyzed degradation of PVC is nonlinear. The equation indicates that the second term in the right-hand side of the equation goes to zero at long times. Thus, at long times, eq. (12) reduces to eq. (10) and the degradation is purely thermal. The rate coefficient for the noncatalytic thermal degradation, k_t, was determined from conducting experiments without catalysts. Thus, there two rate coefficients, k_a and k_c, that are to be determined from the experimental data. The rate coefficient for the consumption of AlCl$_3$ follows an Arrhenius relationship[8] given by $\ln k_a = 3.6127 - 3121/T$, where T is temperature in K. This is substituted in eq. (12) and the rate coefficient k_c was determined by nonlinear regression from the variation

of $[(M_{no}/M_n) - 1]$ with reaction time (Fig. 3). The symbols denote the experimental data while the lines are obtained from the regression. As seen in Figure 3, the prediction by the model is satisfactory and clearly shows that AlCl$_3$ catalyzes the reaction initially but has no effect at long times. The temperature dependence of the rate coefficient k_c is shown in the Arrhenius plot (Fig. 2). The activation energy obtained from the slope of the plot is 43.7 kcal/mol.

CONCLUSION

The catalytic degradation of poly(vinyl chloride) (PVC) in solution was investigated at various temperatures. The time evolution of the molecular weight distribution of the polymer was determined. The degradation kinetics was modeled, and it was determined that the rate coefficients for degradation was higher for the catalytic degradation of PVC when compared to the rate coefficients for the thermal degradation. The activation energy was determined from the temperature dependence of rate coefficients. It was found that the activation energy increased in the presence of a catalyst. This indicates that the catalytic degradation may be occurring by a different mechanism with different rate-controlling steps compared to the thermal degradation mechanism.

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