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KINETICS OF THE THERMAL DEHYDROCHLORINATION OF VINYLIDENE CHLORIDE BARRIER POLYMERS

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Vinylidene chloride copolymers containing a predominance of vinylidene chloride (85–90%) have long been important barrier polymers widely used in the plastics packaging industry. These materials display excellent barrier to the ingress of oxygen and other small molecules (to prevent food spoilage) and to the loss of food flavor and aroma constituents (to prevent flavor scalping on the supermarket shelf). While these polymers have many outstanding characteristics, which have made them commercial successes, they tend to undergo thermally-induced degradative dehydrohalogenation at process temperatures. The dehydrochlorination occurs at moderate temperatures (120–200°C) and is a typical chain process involving initiation, propagation and termination phases. Defect structures, namely internal unsaturation (allylic dichloromethylene groups), serve as initiation sites for the degradation. These may be introduced during polymerization or during subsequent isolation and drying procedures. If uncontrolled, sequential dehydrohalogenation can lead to the formation of conjugated polyene sequences along the polymer mainchain. If sufficiently large, these polyenes absorb in the visible portion of the electromagnetic spectrum, and give rise to discoloration of the polymer. The dehydrochlorination process may be conveniently monitored by thermogravimetric techniques. Both initiation and propagation rate constants may be readily obtained.

Keywords: *activation parameters, analytical methods, kinetics, polymer degradation, vinylidene chloride barrier polymers*

Introduction

Vinylidene chloride copolymers have been commercially used because these polymers have low permeability to oxygen and flavor/aroma constituents such that food quality is maintained in packaging prepared from these materials [1–3]. These polymers are generally free of the defect sites characteristic of similar vinyl polymers, i.e., they are regular head-to-tail, unbranched and highly crystalline polymers [4]. However, when subjected to thermal stress, these polymers undergo degradative dehydrochlorination. This thermal dehydrochlorination is a typical radical chain process with distinct initiation, propagation and termination phases (Fig. 1).[4, 5, 9]. Initiation of degradation is promoted by the presence of any variety of agents capable of introducing random double bonds into the polymer main chain [4]. Unsaturation in these polymers appears to be a principal defect structure (allylic dichloromethylene units) responsible for degradation [4–5]. Thermal homolysis of an allylic carbon-chlorine bond generates a tight carbon chlorine radical pair. The chlorine atom most generally abstracts an adjacent hydrogen atom to extend the unsaturation by one unit, to regenerate an allylic dichloromethylene group, and to propagate the dehydrochlorination reaction. This is illustrated in Scheme 1.

Thermogravimetry continues to be a popular method for the study of polymer degradation [6, 7].

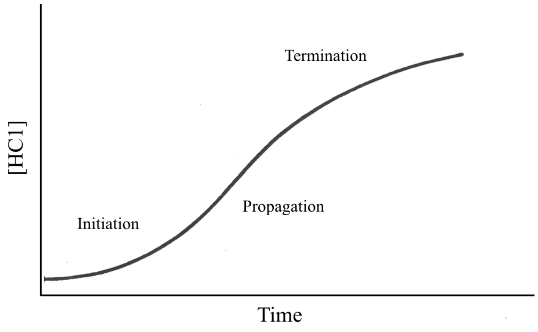
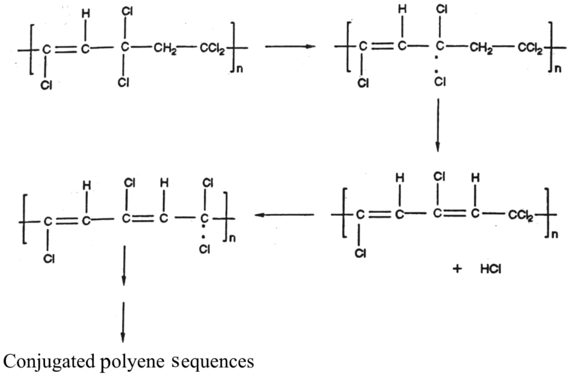


Fig. 1 Hydrogen chloride evolution for the thermal degradation of a typical vinylidene chloride polymer



Scheme 1 Mode of degradation of vinylidene chloride polymers

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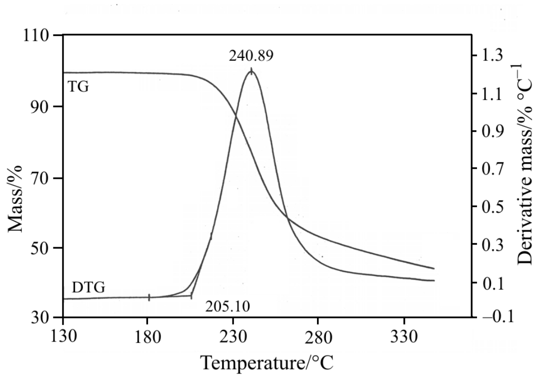

Fig. 2 TG/DTG curves for the degradation of a typical vinylidene chloride polymer

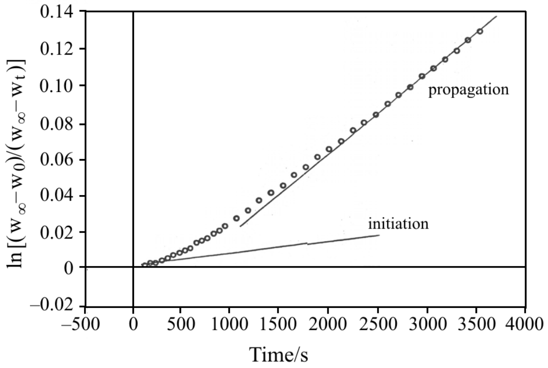

Fig. 4 Thermal degradation of a typical vinylene chloride polymer at 180°C

This reaction is well suited for study by thermogravimetry since the only process occurring at modest temperatures (120–200°C) is the loss of hydrogen chloride, i.e., no other volatile products are formed at these temperatures [8]. Therefore, the rate of change of sample mass accurately reflects the rate of degradation. A thermogram for degradation of a typical vinylidene chloride polymer as a function of temperature is shown in Fig. 2. As can be seen, degradation becomes prominent as the temperature approaches 200°C and occurs smoothly to reflect the loss of hydrogen chloride from each vinylidene chloride per unit in the polymer. The curve for isothermal degradation of the same polymer at 180°C is displayed in Fig. 3. Both the initiation and propagation phases of the degradation are apparent in this plot. These regions are even more obvious in a plot of ln $[(w_\infty - w_0)/(w_\infty - w_t)]$ *vs.* time where w_∞ is the mass of the sample at infinite time (t_∞) taken as that mass remains after 37.62% of the initial vinylidene chloride component mass (corresponding to the complete loss of one mole of hydrogen chloride per vinylidene chloride unit in the polymer) has been lost; w_0 is the mass at time zero (t_0), i.e., the time at which the first data point was recorded and w_t is the mass at any time t, during the run. This is illustrated in Fig. 4. Rate constants for both initiation (k_i) and propagation (k_p) may be obtained from the appropriate linear portions of this plot.

This is illustrated in Figs 5 and 6 in which portions of the data presented in Fig. 4 are replotted. It might be noted that an excellent least squares fit is obtained in both cases. In practice, data for multiple runs are plotted and the average reported as the rate constant [1, 4, 5, 8, 10–12]. This permits a ready assessment of the uncertainty in the value for the rate constant. Reproducibility is typically excellent (Table 1). Determination of rate constants at several temperatures provides the data needed for the construction of a plot of ln(k/t) *vs.* 1/t (where k is the rate constant and T is the corresponding Kelvin temperature) and the extraction of the enthalpy of activation (ΔH^*). Rate constants for the thermal degradation of vinylidene chloride/methyl acrylate (five mole percent) at four different temperatures are shown in Table 1 [13].

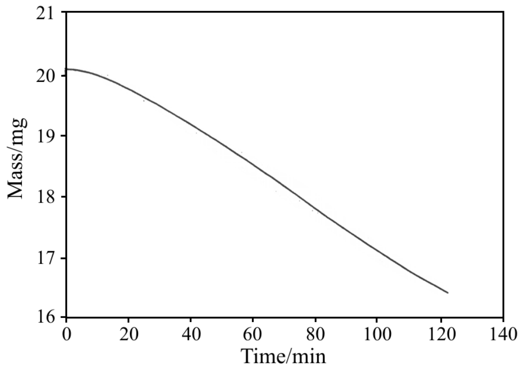

Fig. 3 Degradation of a typical vinylidene chloride polymer at 180°C

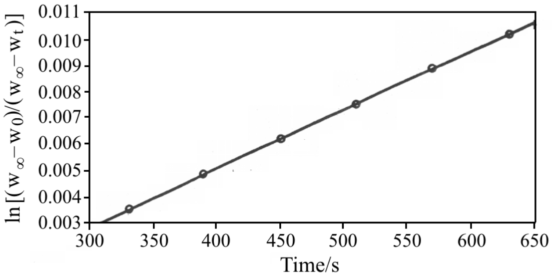

Fig. 5 Initiation rate constant (k_i) for the thermal degradation of typical vinylidene chloride polymer 180°C

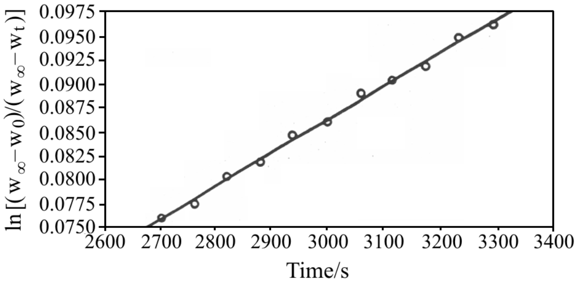

Fig. 6 Propagation rate constant (k_p) for the thermal degradation of a typical vinylidene chloride polymer 180°C

Table 1 Rate constants for the thermal degradation of vinylidene chloride/methyl acrylate (5 mol%) copolymer

$k_i \cdot 10^5/\text{s}^{-1}$ [a,c]	$k_p \cdot 10^5/\text{s}^{-1}$ [b,c]	Temperature/°C
1.55±0.04	2.09±0.06	170
3.31±0.14	4.27±0.14	180
6.26±0.07	8.96±0.10	190
12.88±0.10	17.41±0.03	200

[a] Rate constant for the initiation of degradation; [b] Rate constant for the propagation of degradation; [c] Averages of three determinations accompanied by the average deviation.

Table 2 Activation parameters for the thermal degradation of vinylidene chloride/methyl acrylate (5 mol%) copolymer

Process	Enthalpy of activation, ΔH^*/kJ mol^{-1} [a]	Entropy of activation, ΔS^*/J mol^{-1} K^{-1} [b]
initiation	118	–73.4
propagation	120.1	–66,5

[a] Based on the uncertainty in the values for rate constants and the temperature control (±0.02°C) possible with the TG unit, the estimated uncertainty in activation values is less than 0.42 kJ mol^{-1}; [b] Calculated from the expression: $\Delta S^*/R = \ln k - 23.760 - 1\text{n}T + \Delta H^*/RT$

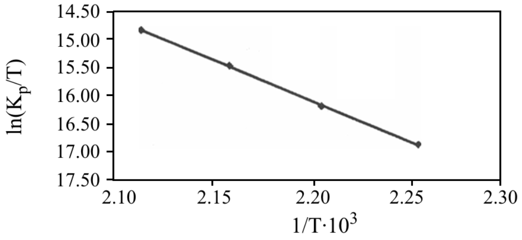

Fig. 7 Activation enthalpy for the propagation of degradation of a standard vinylidene chloride/methyl acrylate (five mole percent) copolymer

A plot of ln(k/T) *vs.* $1/T$ for the propagation reaction is shown in Fig. 7. The slope of this plot is –14480/T and reflects –ΔH^*/R. The activation enthalpy for the initiation reaction may be obtained in an analogous manner. The activation parameters for both the initiation and propagation reactions are collected in Table 2.

Conclusions

The kinetics of the thermally induced degrative dehydrochlorination of vinylidene chloride copolymers may conveniently be studied using thermogravimetry. Rate constants for both initiation and propagation of the dehydrochlorination reaction may be obtained from thermogravimetric data. Determination of the respective rate constants at several different temperatures permits the extraction of a reliable value for the corresponding activation enthalpies. The activation enthalpy for the initiation of degradation was determined to be 118 kJ mol^{-1} while that for propagation is 120.1 kJ mol^{-1}.

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