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STABILITY OF VINYLIDENE CHLORIDE COPOLYMERS CONTAINING 4-VINYLPYRIDINE UNITS

Thermogravimetric assessment

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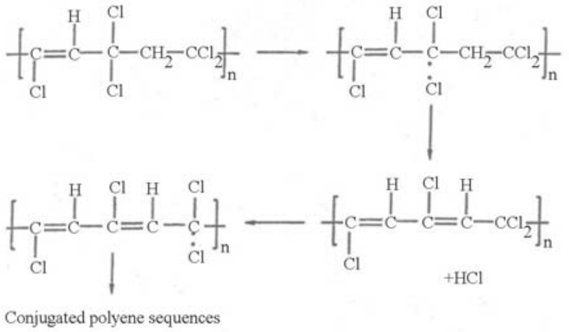
Vinylidene chloride copolymers are prominent in the barrier plastic packaging industry. These materials display excellent barrier to the transport of oxygen (and other small molecules) as well as flavor and aroma molecules. However, they suffer from a propensity to undergo degradative dehydrochlorination at process temperatures. To scavenge hydrogen chloride formed and prevent its interaction with the metallic components of process equipment, a passive base is usually included as an additive prior to processing. The base is most often an inorganic oxide or salt. These may negatively impact the properties of the polymer, particularly as a film. An organic base that could be covalently incorporated into the copolymer might display better behavior. Accordingly, a series of copolymers containing low levels of 4-vinylpyridine (0.05–3 mole%) have been prepared, characterized, and examined by thermogravimetry to assess thermal stability. In all cases, polymers containing 4-vinylpyridine units are less stable than the polymer containing none of this comonomer. Clearly, the pyridine moiety is a sufficiently strong base to promote E2 elimination of hydrogen chloride to generate dichloromethylene units in the mainchain from which thermal degradation may be initiated.

Keywords: *plastic packaging, thermogravimetry, vinylidene chloride copolymers*

Introduction

Vinylidene chloride copolymers are prominent in the barrier plastic packaging industry [1]. The permeability of oxygen (and other small molecules) as well as flavor and aroma compounds in these polymers is extremely low. Thus packaging containing these polymers as a functional component prevents spoilage of food items as well as 'flavor scalping' during warehouse storage and supermarket display. While these polymers have very desirable properties for the construction of packaging they must be processed with care at relatively low temperatures (l50–170°C) in specially designed equipment. This limitation arises from the propensity for these polymers to undergo thermally-induced degradative dehydrochlorination at the melt temperature [2]. This process has two deleterious effects which must be controlled. If unchecked, successive dehydrochlorination along the polymer mainchain will lead to the formation of polyene sequences large enough to absorb in the visible portion of electromagnetic spectrum and impart color to the material (Scheme 1).

A second impact of this degradation is the evolution of hydrogen chloride which can interact with the walls of process equipment to form metal halides, particularly iron chlorides, which act as Lewis acid catalysts to strongly promote the dehydrochlorination reaction [3]. To prevent this, a passive base capable of absorbing hydrogen chloride must be present in the polymer melt either as an additive or as an integral part of the polymer.



Scheme 1 Mode of degradation of vinylidene chloride polymers

Experimental

Materials and methods

Polymers

Copolymers of vinylidene chloride containing a constant 5 mole% methyl acrylate and small but varying amounts of 4-vinylpyridine were prepared by suspension polymerization using AIBN as initiator

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and methods previously described [2]. In all cases, the mass average molecular mass of the polymers (SEC) was approximately 100000 with a polydispersity of about two. Analysis of the polymers by carbon-13 NMR spectroscopy established that the expected level of comonomer(s) had been incorporated [4].

Instrumentation

Polymers were characterized by spectroscopic, thermal, and chromatographic methods [5]. Differential scanning calorimetry (DSC) was carried out at a heating rate of 5°C min^{-1}, using a TA Instruments Inc. model 2100 thermal analysis system equipped with a model 2910 DSC cell. The sample compartment was exposed to a constant purge of dry nitrogen at 50 mL min^{-1}. Thermogravimetry was accomplished using a TA Instruments model 2950 TGA unit interfaced with the 2100 control module. The TG cell was swept with nitrogen at 50 mL min^{-1} during degradation runs. The sample size was 5–10 mg in a platinum sample pan. Both DSC and TG instruments were calibrated using the protocol prescribed by the manufacturer. Size exclusion chromatography (SEC) was accomplished using solutions in tetrahydrofuran, microstyrogel columns, and linear poly(styrene) calibration. Nuclear magnetic resonance (NMR) spectra were obtained using a General Electric NT-30 spectrometer and samples dissolved in tetrahydrofuran (THF). The data acquisition parameters for ^{13}C NMR spectra obtained at 75.5 MHz were a pulse width of 90°, a delay time of 10 s, a size of 16 K, an accumulation time of 0.41 s, a sweep width of 20 KHz, exponential apodisation, 5 Hz line broadening, and gated decoupling without NOE (Nuclear Overhauser Effect).

Assessment of polymer stability

A direct reflection of the thermal stability of the polymers, i.e., the propensity to undergo degradative dehydrochlorination was obtained by thermogravimetry [6, 7]. A comparison of curves obtained by ramping the temperature from 30–170°C provided an indication of the relative stability of the polymers. This was also reflected in the extrapolated onset temperature for degradation in each case. Rate constants for the degradative dehydrochlorination were obtained from isothermal experiments. For isothermal kinetic studies the temperature was rapidly ramped to a fixed temperature between 120 and 180°C and allowed to equilibrate three minutes before data acquisition was begun.

Results and discussion

Vinylidene chloride copolymers undergo degradative dehydrohalogenation at process temperatures. To scavenge hydrogen chloride formed, the stabilization system for these polymers generally contains a passive base. Often this is a maingroup metal oxide or a polyvalent oxyanion salt. The presence of these inorganic stabilizers may contribute negatively to the clarity of the finished product. For this reason organic stabilizers which would be compatible with the polymer, which would effectively absorb evolved hydrogen chloride, and which would not actively promote the dehydrochlorination reaction have been sought. Amines, even highly hindered amines, have been found to be too basic to function as satisfactory stabilizers [8, 9]. The incorporation of a comonomer containing a basic site into these polymers could eliminate the need for a stabilizing additive. In this case vinylidene chloride copolymers containing a constant 5 mole% methyl acrylate and small but varying amounts of 4-vinylpyridine have been prepared, characterized, and subjected to thermogravimetry to assess thermal stability. The results are displayed below in Fig. 1. As can be seen the presence of even small levels of 4-vinylpyridine units in the polymer has a strongly deleterious impact on its thermal stability. All the polymers containing 4-vinylpyridine are less stable than the standard vinylidene chloride/methyl acrylate (5 mole%) copolymer. The polymer containing 3% 4-vinylpyridine is dramatically less stable with degradation onset at about 130°C. Decomposition data for all the polymers are collected in Table 1.

This thermal dehydrochlorination is a typical radical chain process with distinct initiation, propagation and termination phases (Fig. 2) [1].

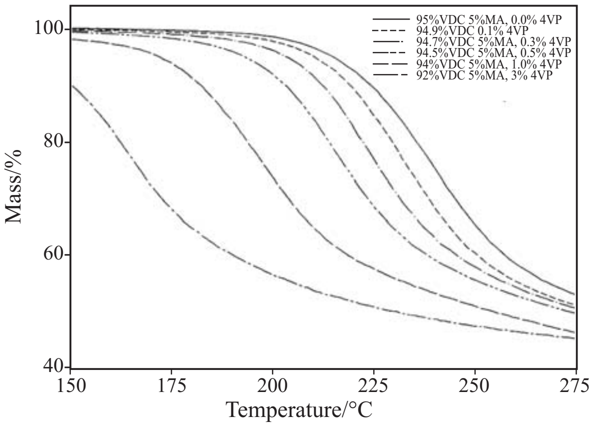

Fig. 1 Thermal degradation of vinylidene chloride/methyl acrylate (5 mole%) copolymers containing varying amounts of 4-vinylpyridine

Table 1 Thermal degradation characteristics of vinylidene chloride/methyl acrylate copolymers containing varying amounts of 4-vinylpyridine

4-vinylpyridine/ mole%	Degradation onset[a]/ °C	Temp. of max. degradation rate[b]/ °C
0	202	241
0.1	200	231
0.3	194	222
0.5	184	215
1	163	296
3	134	165

[a]Extrapolated onset temperature from the derivative plot of mass loss *vs.* temperature; the reproducibility for multiple determinations is ±0.2°C, [b]Maximum in the derivative plot of mass loss *vs.* temperature; the reproducibility for multiple determinations is ±0.1°C

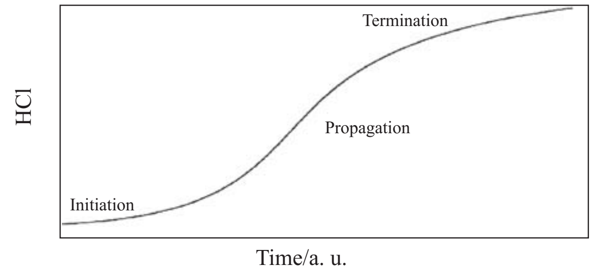

Fig. 2 Hydrogen chloride evolution for the thermal degradation of a typical vinylidene chloride polymer

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. 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 [10, 11]. Therefore, the rate of change of sample mass accurately reflects the rate of degradation of a typical vinylidene chloride polymer as a function of temperature. Degradation becomes prominent as the temperature approaches 200°C and occurs smoothly to reflect the loss of hydrogen chloride from each vinylidene chloride mer 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 (w_t) taken as that mass which 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.

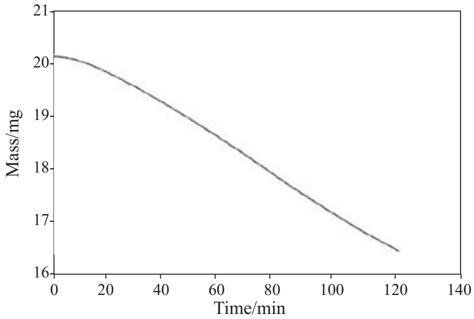

Fig. 3 Degradation of a typical vinylidene chloride polymer at 180°C

Data from the appropriate portions of this plot for the thermal decomposition of a vinylidene chloride/methyl acrylate (5 mole%)/4-vinylpyridine (0.1 mole%) terpolymer are replotted in Figs 5 and 6.

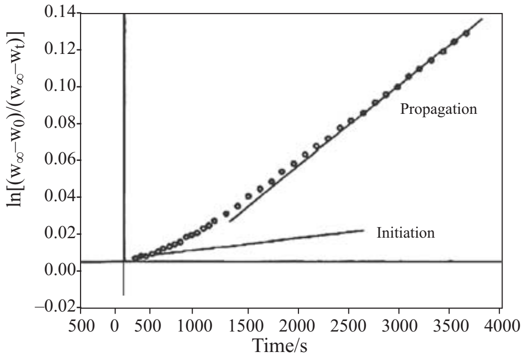

Fig. 4 Thermal degradation of a typical vinylene chloride polymer at 180°C

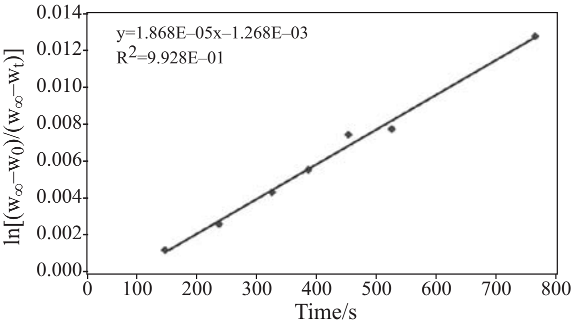

Fig. 5 Initiation rate constant (k_i) for the thermal degradation of a vinylidene chloride/methyl acrylate (5 mole%)/4-vinylpyridine (0.1 mole%) terpolymer at 170°C

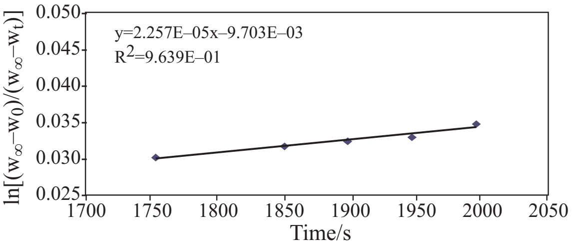

Fig. 6 Propagation rate constant (k_p) for the thermal degradation of a vinylidene chloride/methyl acrylate (5 mole%)/4-vinylpyridine (0.1 mole%) terpolymer at 170°C

Table 2 Rate constants for the thermal degradation of vinylidene chloride/methyl acrylate (5 mole%)/4-vinylpyridine (variable content) terpolymers at 170°C

4-vinylpyridine/ mole%	$k_i \cdot 10^5/s^{-1a,c}$	$k_p \cdot 10^5/s^{-1b,c}$
0	1.54±0.02	2.07±0.04
0.1	1.86±0.01	2.26±0.01
0.3	20.15±0.10	25.25±0.2
0.5	46.44±0.3	54.60±0.10
1	–	240.03±3.00

[a]Rate constant for the initiation of degradation, [b]Rate constant for the propagation of degradation, [c]Average of three determinations accompanied by the average deviation

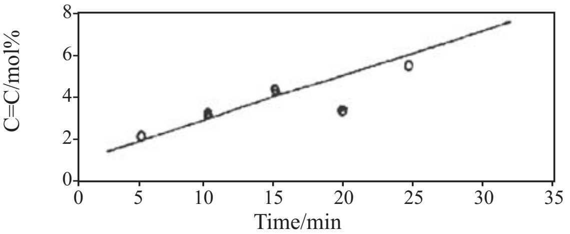

Fig. 7 Increase in unsaturation in a vinylidene chloride/ 4-vinylpyridine (12 mole%) copolymer undergoing thermal degradation at 100°C

Figure 5 represents a plot of ln mass change *vs.* time for the early portion of the degradation in which initiation is occurring. An excellent linear plot is obtained for which the slope reflects the rate constant, k_i, for the initiation of degradation. Similarly, the corresponding plot (Fig. 6) of data at long reaction time allows the extraction of k_p, the rate constant for propagation of the degradation reaction. Multiple determinations were carried out and in all cases excellent reproducibility was observed. The rate constants for the degradation at 170°C of the series of polymers containing varying levels of 4-vinylpyridine are tabulated in Table 2.

It is readily apparent that the presence of 4-vinylpyridine units in the polymer negatively impacts the stability of the polymer. This is fully consistent with the results obtained by NMR analysis of samples which had been oven aged at 100°C for varying lengths of time [4]. The level of unsaturation in the polymer increases regularly as a function of time at 100°C. This is illustrated in Fig. 7. The fact that the thermal degradation of these polymers is so facile at relatively modest temperature suggests that the pyridine moiety is sufficiently basic so as to promote E2 elimination in vinylidene chloride sequences to generate initiation sites (internal unsaturation; allylic dichloromethylene units) for the thermal dehydrochlorination.

Conclusions

Vinylidene chloride/4-vinylpyridine copolymers undergo facile thermally-promoted degradative dehydrochlorination. The pyridine moiety in the comonomer units of the polymers is sufficiently basic so as to actively strip hydrogen chloride from vinylidene chloride units to generate initiation sites for the thermal reaction.

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