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Thermal degradation characteristics of vinylidene chloride/2-[3,4-(1,1-dioxycyclopentyl)phenyl]ethyl acrylate copolymers¹

B.A. Howell*, B.B.S. Sastry, S.I. Ahmed, P.B. Smith

Center for Applications in Polymer Science, Central Michigan University, Mt. Pleasant, MI 48859, USA

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Abstract

Vinylidene chloride copolymers form the base for a significant segment of the barrier plastic packaging industry. While these materials have many superior properties they tend to undergo degradative dehydrochlorination at process temperatures. In an attempt to identify polymers which might display increased thermal stability, a series of vinylidene chloride/2-[3,4-(1,1-dioxycyclopentyl)phenyl]ethyl acrylate copolymers has been examined by thermogravimetry. These polymers contain a 3,4-dihydroxyphenyl pendant masked as the cyclopentanone ketal. In principle, this moiety could consume evolved hydrogen chloride (to prevent its interaction with the walls of process equipment) to expose phenolic groups which might scavenge chlorine atoms. Both processes should enhance the stability of the polymeric system. In practice, copolymers containing 1.2, 2.6, 4.2 and 4.9 mol% 2-[3,4-(1,1-dioxycyclopentyl)phenyl]ethyl acrylate all undergo thermal degradation at approximately the same rate. The rate of decomposition of these copolymers, as reflected in both the rate constants (k_i) for initiation and propagation (k_p) of the degradation reaction, is not significantly different from that of the vinylidene chloride homopolymer.

Keywords: Degradation; Vinylidene chloride copolymer; TG

1. Introduction

Vinylidene chloride copolymers occupy a place of prominence in the barrier plastics packaging industry [1,2]. These materials exhibit a high barrier to the transport of oxygen

* Corresponding author.

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and other small molecules as well as flavor and aroma agents [1–3]. The copolymers of vinylidene chloride with alkyl acrylates are particularly useful in these applications [4]. When subjected to the temperatures necessary for processing, these polymers undergo degradative dehydrochlorination [4]. This thermally induced dehydrochlorination is a typical radical chain process with distinct initiation, propagation and termination phases [5–7]. Elimination of hydrogen chloride introduces unsaturation into the polymer main-chain and generates an allylic dichloromethylene unit. Further dehydrohalogenation then may occur readily via an allylic radical, chlorine atom pair. Unchecked, this propagation of the dehydrochlorination reaction leads to the formation of polyene sequences which often impart objectionable color to the polymer [4]. Several approaches to the stabilization of these polymers have been explored [8]. These have involved, in the main, utilization of a passive base to trap evolved hydrogen chloride, a free-radical stabilizer to scavenge chlorine atoms, or a nucleophilic agent to remove allylic chlorine from the polymer mainchain [3]. Incorporation of 2-[3,4-(1,1-dioxycyclopentyl)phenyl]ethyl acrylate (DHPEA) into a vinylidene chloride polymer offers the potential for two modes of stabilization. The DHPEA monomer is a 2-phenylethyl acrylate with hydroxyls at the 3,4-positions of the phenyl group masked as the cyclopentanone ketal. Evolved hydrogen chloride might be scavenged by reaction with the ketal functionality. This would, in turn, expose two phenolic groups which could act as free radical stabilizers to scavenge free chlorine atoms that might be present as a consequence of the ongoing degradation. Thermoxidative reactions at the methylene group in the mainchain (generally less important than dehydrohalogenation for these polymers) should also be suppressed by the presence of the phenolic functionality.

2. Experimental

2.1. Materials

Vinylidene chloride/2-[3,4-(1,1-dioxycyclopentyl)phenyl]ethyl acrylate (VDC/DHPEA) copolymers containing 1.2, 2.6, 4.2 and 4.9 mol% DHPEA were prepared by suspension polymerization as previously described using hydroxymethyl cellulose as suspending agent and AIBN as initiator [9]. The random sequence distribution and compositions for the polymers were established using ^{13}C NMR spectroscopy and methods previously established [10]. Spectra were recorded using solutions in *o*-dichlorobenzene at 120°C and a Bruker AC-300 instrument operating at 75 MHz. Molecular weights for the polymers were determined by size exclusion chromatography using solutions in 1,3,5-trichlorobenzene at 130°C, microstyrogel columns, and linear polystyrene calibration. The results are displayed in Table 1.

2.2. Thermal degradation

The thermal degradation characteristics of VDC/DHPEA copolymers containing 0.0, 1.2, 2.6, 4.2 and 4.9 mol% DHPEA were examined by thermogravimetry using a TA Instruments model 2950 TGA unit interfaced with the TA Instruments Thermal Analyst

Table 1
Molecular weights for VDC/DHPEA copolymers^a

Sample	Mol% DHPEA	M_n	M_w	M_z	M_w/M_n
1	1.2	46000	221000	724000	4.78
2	2.6	36000	181000	720000	4.99
3 ^b	4.2	12000	43000	135000	3.63
4 ^b	4.9	33000	124000	485000	3.81

^aDetermined by size exclusion chromatography using solutions in TCB at 130°C, microstyrogel columns, linear polystyrene calibration, and refractive index detection.

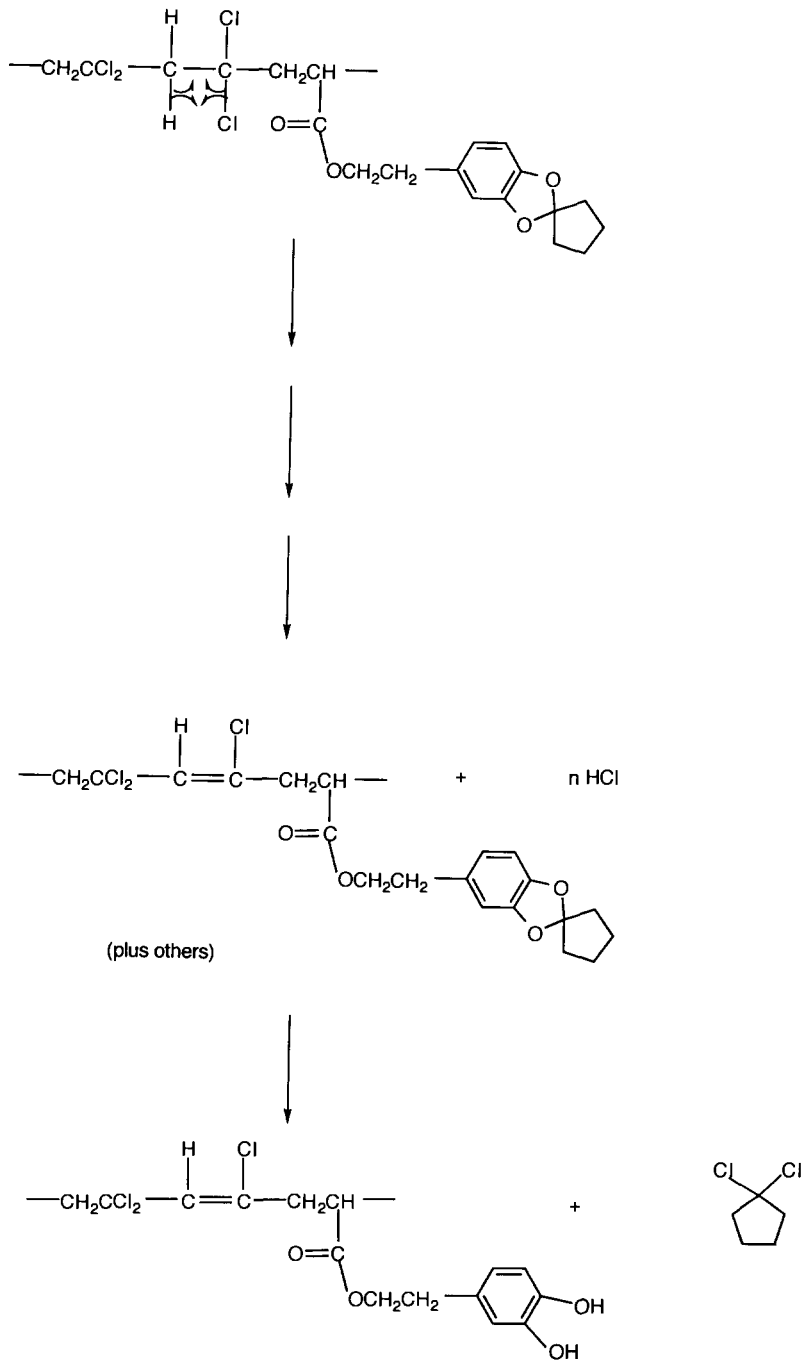
^bIncompletely soluble in TCB at 130°C.

2100 control unit. Decay plots, weight loss versus time (or temperature) were generated by feeding the analyzer output (TA Instruments software was used for all data manipulation) to a model 7440 Hewlett-Packard plotter. The TGA cell was swept with nitrogen at 50 ml min⁻¹ during degradation runs and the sample, approximately 20 mg, was contained in a platinum sample pan. For dynamic runs, the temperature was ramped at a rate of 5°C min⁻¹ from 30°C to 350°C. For isothermal runs, the temperature of the cell was rapidly brought to 180°C (with the TA Instruments high intensity cell about 2 min was required for temperature equilibration) and weight loss was monitored as a function of time for at least two half-lives.

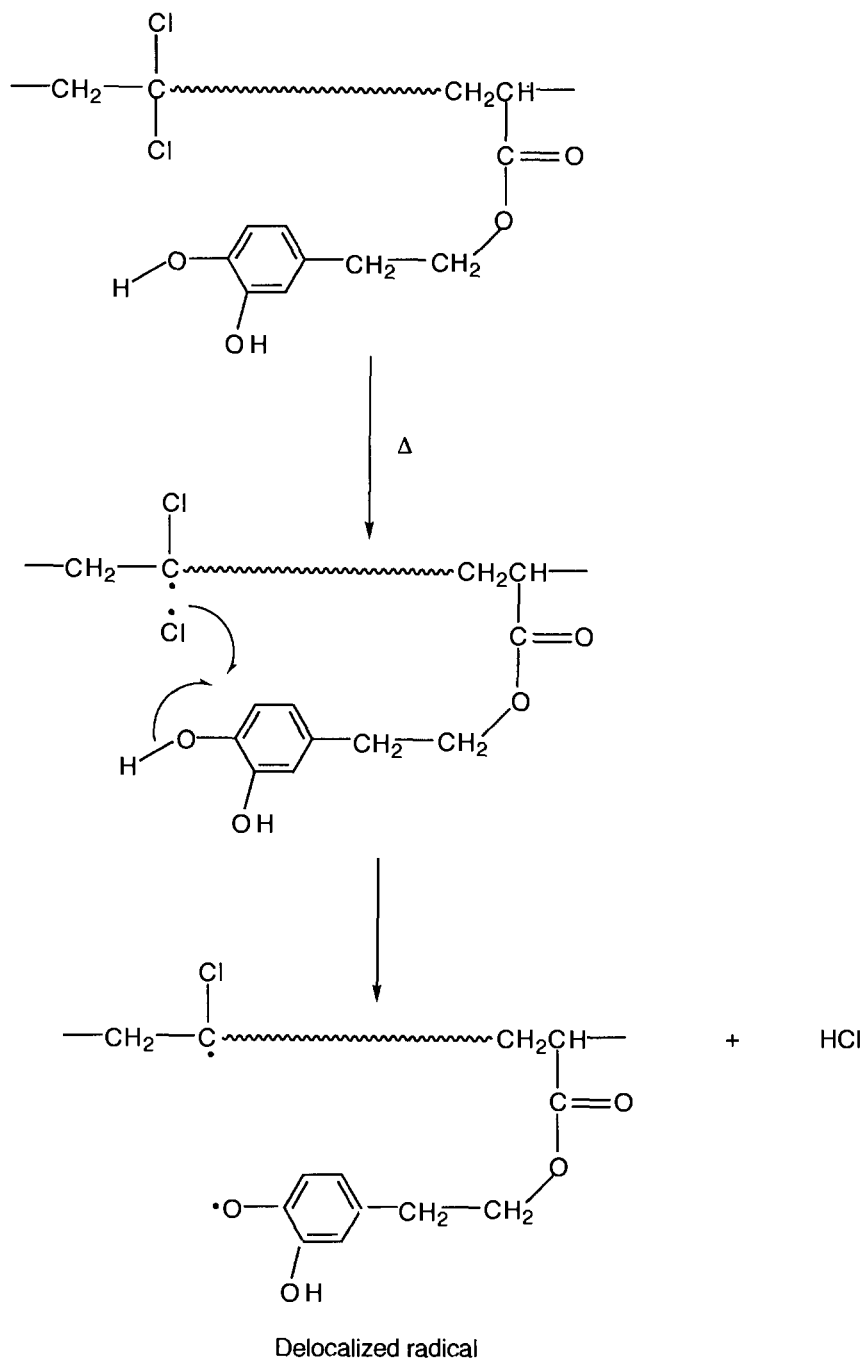
3. Results and discussion

A vinylidene chloride/acrylate copolymer of enhanced thermal stability would be immediately beneficial to the food packaging industry. Vinylidene chloride/alkyl acrylate copolymers afford a high barrier to the transport of oxygen and flavor and aroma molecules. However, at process temperatures these materials tend to undergo degradative dehydrochlorination. Potentially, this degradation could be controlled by use of an acrylate comonomer capable of (1) reaction with evolved hydrogen chloride to remove it from the system and prevent interaction with process equipment walls to produce metal halides which function as Lewis acids to catalyze the degradation and (2) scavenging free chlorine atoms or other reactive radical species. Incorporation of DHPEA as comonomer introduces the possibility for both modes of stabilization. As depicted in Scheme 1, cleavage of the ketal function by evolved hydrogen chloride would not only consume hydrogen chloride but would expose phenolic groups which could function as free-radical scavengers.

Initial thermally induced dehydrochlorination would generate hydrogen chloride. Reaction of evolved hydrogen chloride with the ketal functionality would consume two moles of hydrogen chloride per acrylate unit in the polymer and would convert these units to catechol-bearing pendants. As shown in Scheme 2, the catechol moiety could function as a typical free-radical stabilizer to scavenge chlorine atoms. In general, free-



Scheme 1. Potential mode for the scavenging of evolved hydrogen chloride by the ketal units in a VDC/DHPEA copolymer.



Scheme 2. Potential scavenging of chlorine atoms by phenolic groups in a vinylidene chloride/(3,4-dihydroxyphenyl)ethyl acrylate copolymer.

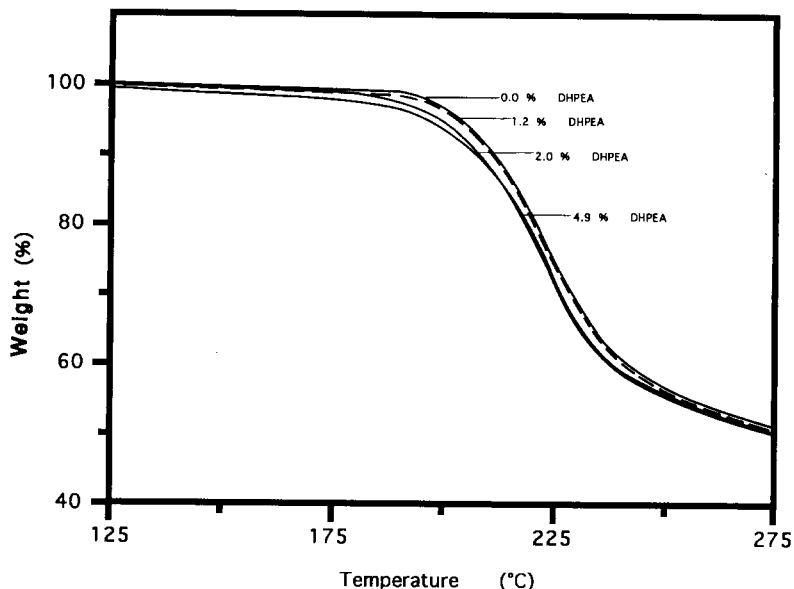


Fig. 1. Thermal degradation of VDC/DHPEA copolymers.

radical scavengers are not very effective as stabilizer additives for vinylidene chloride copolymers [11]. However, in this case the phenolic groups are intimately associated with the polymer as comonomer and might be expected to be somewhat more effective.

To test this notion, VDC/DHPEA copolymers containing 0.0, 1.2, 2.6, 4.2 and 4.9 mol% DHPEA were prepared by suspension polymerization, characterized spectroscopically, and subjected to examination by thermogravimetry. Plots of weight loss versus temperature for these materials are displayed in Fig. 1.

It is apparent from these qualitative comparisons that incorporation of DHPEA into the mainchain has little impact on the overall stability of the polymer. In fact, all the copolymers undergo degradation somewhat more readily than does the VDC homopolymer.

Table 2

Rate constants for the thermal degradation of VDC/DHPEA copolymers at 180°C

Sample	Mol% DHPEA	$k_i (\times 10^4)/s^{-1}$ ^a	$k_p (\times 10^4)/s^{-1}$ ^b
0	0.0	1.46 ± 0.12	2.49 ± 0.24
1	2	1.47 ± 0.26	2.92 ± 0.39
2	2.6	1.52 ± 0.33	2.66 ± 0.63
3	4.2	—	—
4	4.9	1.68 ± 0.73	2.36 ± 0.89

^aInitiation rate constant; values are averages from at least two runs.

^bPropagation rate constant; values are averages from at least two runs.

These initial observations are substantiated by the rate constants for degradation found in Table 2. Both the rate constants for the initiation of degradation (k_i) and its propagation (k_p) are very similar and independent of the acrylate content of the copolymer. The level of acrylate is always small, never more than 5 mol%, so that the impact of its presence might be expected to be small. However, even if the projected stabilization modes were not operable, a positive impact on stability would be expected to arise from interruption of the VDC sequences alone [12]. Degradation would appear to be occurring in the VDC sequences unimpeded by the presence of acrylate units. This may be suggestive of significant chain transfer/crosslinking at the acrylate units during polymerization. That substantial crosslinking may have occurred is reflected in the sparing solubility of the copolymers in 1,3,5-trichlorobenzene at 130°C, particularly for the samples containing larger amounts of DHPEA. In any case, evolved hydrogen chloride would appear not to be consumed by reaction with the ketal functionality of DHPEA under the conditions of thermogravimetry. This is consistent with earlier results which suggest that anhydrous hydrogen chloride in a solid polymer matrix is not sufficiently vigorous to cleave a ketal, i.e. a more reactive moiety may be needed to scavenge evolved hydrogen chloride under these conditions [13].

4. Conclusions

Incorporation of an acrylate comonomer containing a phenolic ketal into vinylidene chloride copolymers offers the potential to provide a unit capable of reaction with hydrogen chloride evolved during thermal degradation of the polymer to expose phenolic groups which might behave as radical traps. Both phenomena should have a stabilizing influence on the polymer. Thermogravimetry of a series of vinylidene chloride copolymers containing varying amounts of DHPEA demonstrates that the stabilizing potential offered by this comonomer is not realized. It is likely that anhydrous hydrogen chloride is incapable of cleavage of the ketal functionality during thermal degradation of the polymer.

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