

Thermogravimetric assessment of the suitability of cyclohexa-2,5-dienecarboxylates as stabilizers for vinylidene chloride polymers

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Abstract

Vinylidene chloride (VDC) copolymers display excellent barrier to the transport of oxygen and other small molecules as well as flavor and aroma constituents of food items. For this reason they occupy a place of prominence in the barrier plastic packaging industry. However, they tend to undergo degradative dehydrochlorination during processing. To prevent the development of objectionable color the degradation reaction must be controlled. The dehydrochlorination reaction is a typical radical chain process with an allylic carbon, chlorine atom radical pair as the chain propagating species. The presence of additives that might interrupt this process by scavenging radical moieties, particularly chlorine atoms, should have a stabilizing influence on the polymer. 1,4-Cyclohexadienes are known to be good hydrogen atom transfer agents. Incorporation of this structure into a compound that is nonvolatile, compatible with the polymer, and approved for food contact might generate an effective stabilizer. Accordingly, 2,5-cyclohexadienecarboxylates have been synthesized and used to prepare blends (1, 5 and 10 wt.%) with a standard VDC/methyl acrylate (9 wt.%) copolymer. The stability of the various blends has been determined by thermogravimetry.

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1. Introduction

Chlorinated polymers, poly(vinyl chloride) (PVC), chlorinated poly(ethylene) (CPE), chlorinated poly(vinyl chloride) (CPVC), and vinylidene chloride (VDC) copolymers—usually with vinyl chloride or alkyl acrylates, make an important contribution to our well-being and to the economies of most developed nations. PVC is the most common chlorinated plastic found in a variety of products such as garden

hoses, tapes, floor tile, and many others. PVC comprises about 15% of the total United States plastics market [1]. Worldwide in 1999, 25 million metric tons of PVC was used (34% for pipes and fittings, 17% for profiles and tubes, 16% for film and sheet, 7% for wire and cable, 3% for bottles, and 23% for other uses) [2]. VDC polymers are used in much smaller volume than is PVC and account for between 0.2 and 2% of the total plastics market. These materials are not commodity plastics but rather are specialties which find application in the barrier plastic packaging industry (PVC sells for about \$ 0.40/lb while most VDC polymers are >\$ 1.50/lb). Therefore, the societal and economic impact of these resins

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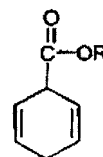
is much larger than it was suggested by volume alone.

VDC 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 [3–5]. 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 [6]. 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 [6–9]. Initiation of degradation is promoted by the presence of any of a variety of agents capable of introducing random double bonds into the polymer main-chain [6]. Unsaturation in these polymers appears to be a principal defect structure (allylic dichloromethylene units) responsible for degradation [6,7]. 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. Several means of potential stabilization of these materials are suggested by this mode of decomposition. For example, the presence of an effective radical (chlorine atom) scavenger might be expected to disrupt propagation of the dehydrochlorination reaction and provide stabilization for the polymer.

1,4-Cyclohexadienes are good hydrogen atom transfer agents. A large driving force for the hydrogen transfer is the conversion of the cyclohexadiene to a fully aromatic benzene derivative. In fact, the transfer is so facile that the cyclohexadienes act as inhibitors for radical polymerizations. Due to this large propensity for the trapping of radical species by hydrogen transfer, the cyclohexadienes might function as effective stabilizers for VDC polymers by scavenging chlorine atoms and other radical species produced by thermal degradation. For VDC polymers to be used in food packaging, stabilizers must not be toxic. Ideally, they should be compounds that have Food and Drug Administration approval for use as food additives. Alkyl substituted 1,4-cyclohexadienes or 1,4-cyclohexadiene itself would not be suitable

stabilizers since they would be converted to benzene or substituted benzenes as a consequence of hydrogen transfer. These compounds, particularly benzene, are known carcinogens and if leaked from packaging into food cause unacceptable health risk. On the other hand, 1,4-cyclohexadienes containing carboxyl or carboxylate ester functional groups would not be subject to this limitation since they would be converted to benzoic acid or benzoic acid esters by hydrogen transfer. Benzoic acid, usually as an alkali metal salt, is a common food additive. It is not toxic to humans because it is readily conjugated with glycine to form hippuric acid which is quite water soluble and is rapidly removed from the biological system via the kidneys and excreted in the urine. For example, 1 or 2% sodium benzoate in bread will prevent mold growth for up to a week or more. Bread without additive will generally grow mold within a day or two.

Because of these considerations a carboxyl-substituted 2,5-cyclohexadiene was selected for synthesis as a potential stabilizer for VDC polymers. The carboxyl derivative can be converted to either benzoic acid itself or benzoic acid esters by hydrogen transfer. From the standpoint of food contamination, the carboxyl-substituted compound would be the most attractive (direct conversion to benzoic acid by hydrogen transfer) but carboxyl esters with long alkyl groups might be expected to be more compatible with the polymer. The general structure of these compounds is shown below.



R = H, Et, Bu, Hex, Oct, Dodec

2. Experimental

2.1. Methods and instrumentation

Additives and polymers were characterized by spectroscopic, thermal, and chromatographic methods. Nuclear magnetic resonance spectra (^1H and ^{13}C) were obtained using a General Electric QE-300 NMR

spectrometer and dilute solutions in deuteriochloroform, perdeuterodimethyl sulfoxide, or perdeuterotetrahydrofuran. Chemical shifts are reported in δ units with respect to internal tetramethylsilane. Infrared (IR) spectra were obtained using solid solutions (1%) in anhydrous potassium bromide (as pellets) or thin films between sodium chloride discs and a model 560 Perkin-Elmer FTIR instrument. Absorption intensities were classified as weak (w), medium (m), strong (s), very strong (vs), stretching (str), and bending (ben). Differential scanning calorimetry (DSC) was carried out at a heating rate of 5 °C/min, 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. Thermal degradation characteristics were obtained by using a TA Instruments Inc. model 2950 TGA unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. The TGA cell was swept with nitrogen at 50 ml/min during degradation runs. The temperature was ramped at a rate of 2–10 °C/min or for isothermal kinetic runs held at a specified temperature. Mass spectra were obtained using a Hewlett-Packard 5995A GC/MS with programmed temperature inlet (90–200 °C) or direct sample insertion with an ionizing potential of 70 eV. UV spectra were recorded using a Hewlett-Packard 8453 UV spectrometer. Samples were dissolved in a suitable solvent at a concentration of 10^{-5} M. Size exclusion chromatography (SEC) was accomplished using solutions in tetrahydrofuran, microstyrogel columns, and linear poly(styrene) calibration.

2.2. Polymer/additive blends

The VDC/methyl acrylate (9 wt.%) copolymer was suspended in a methylene chloride solution of the appropriate amount of 2,5-cyclohexadienecarboxylic acid or alkyl ester (amounts sufficient to provide 1, 5 and 10% by weight of the blend). The suspension was stirred on a rotary evaporator for 0.25 h. The solvent was removed by rotary evaporation at reduced pressure and the blend was then dried at reduced pressure (20 Torr) and 50 °C overnight. As an example, 0.50 g of 2,5-cyclohexadienecarboxylic acid was dissolved in 50 ml of methylene chloride in a round-bottomed flask. Polymer, 9.5 g was added and the mixture was stirred for 15 min. The solvent was removed by rotary

evaporation at reduced pressure. The blend was transferred to a Pyrex dish and dried at 20 Torr and 50 °C overnight.

2.3. Polymer pretreatment with additive

A solution of the appropriate amount of 2,5-cyclohexadienecarboxylic acid derivative in chlorobenzene was placed in a dry round-bottomed flask fitted with a magnetic stirring bar and a Liebig condenser bearing a gas-inlet tube. The temperature of the solution was increased to approximately 130 °C (external heating) and the appropriate amount of polymer was added. The solution was then stirred at 130 °C (solvent reflux) for 2 h. The solution was allowed to cool to approximately 40 °C and slowly poured into cold methanol. The polymer blend precipitated was collected by filtration at reduced pressure. The polymer blend was re-dissolved in chlorobenzene and precipitated again in methanol, collected and dried overnight at 50 °C and reduced pressure (20 Torr).

2.4. Assessment of stability of polymer/additive blends

The thermal degradation of blends of a standard VDC/methyl acrylate (9 wt.%) copolymer with various amounts of selected 2,5-cyclohexadienecarboxylates was observed using a TA Instruments model 2950 TGA unit interfaced with a TA Instruments Thermal Analyst 2100 control unit. Samples (6–15 mg) were loaded onto a platinum sample pan. In a typical run, the TGA cell was swept with nitrogen at 50 ml/min for 30 min prior to the beginning and during data collection. Weight loss was plotted as either a function of temperature or time (isothermal degradation). A 5 °C/min ramp rate was used; isothermal decomposition was observed at 180 °C using the isotherm feature (temperature controlled on oven thermocouple) of the Thermal Analyst 2100 software. Ramp experiments were used to observe qualitative differences in initiation and propagation of degradative dehydrochlorination as a function of the amount of 2,5-cyclohexadienecarboxylate loaded. Isothermal runs were used to obtain first order rate constants for initiation and propagation of dehydrohalogenation. Rate constants were taken as the slopes of the appropriate linear portions of a plot of

$\ln((w_\infty - w_0)/(w_\infty - w_t))$ versus time, where w_∞ is the weight of the sample at infinite time (t_∞) taken as that weight that remains after 37.62% of the initial VDC component weight (corresponds to the complete loss of 1 mol of hydrogen chloride per VDC unit in the polymer) had been lost; w_0 the weight at time zero (t_0), i.e., the time at which the first point was recorded; w_t the weight at any time t , during the run.

2.5. Additives

2.5.1. 2,5-Cyclohexadienecarboxylic acid

Into a dry, 1000 ml, three-necked, round-bottomed flask fitted with a gas-inlet tube extending to the bottom of the flask, a Trubore stirrer, and a cold-finger-type dry-ice condenser was placed 20.1 g (0.164 mol) of benzoic acid and 150 ml of anhydrous, peroxide-free tetrahydrofuran (distilled from lithium aluminum hydride prior to use). The solution was cooled (external dry-ice/acetone bath) and 600 ml of liquid ammonia was introduced via the gas-inlet tube extending to the bottom of the flask. The gas-inlet tube was removed and 4.3 g of lithium (freshly cut lengths of lithium wire) was added portionwise over a period of 1.5 h. After the addition of lithium was complete, the mixture was stirred for 6 h. Ethanol (200 ml) was then added dropwise followed by the portionwise addition of 60 g of ammonium chloride. The mixture was stirred vigorously for 1 h and then allowed to stand for evaporation of the ammonia. The residue was treated with 200 ml of water and sufficient 10% aqueous hydrochloric acid solution to bring the pH of the mixture to 3–4. The resulting solution was extracted with four 200-ml portions of diethyl ether. The extracts were combined, washed with two 100-ml portions of saturated aqueous sodium chloride solution, and dried over anhydrous magnesium sulfate. The solvent was removed from the ether solution by rotary evaporation at reduced pressure. Evaporation at 1–2 Torr was continued until a constant residual weight was achieved. The clear, colorless residual liquid (18.9 g, 93.1% yield) was characterized by DSC and spectroscopy: m.p. 17 °C; ^1H NMR (δ , CDCl_3) 2.73 (m, 2H, methylene protons), 3.78 (m, 1H, methine proton), 5.84 (m, 2H, vinyl protons), 5.90 (m, 2H, vinyl protons); ^{13}C NMR (δ , CDCl_3) 25.8 (methylene carbon atom), 41.5 (methine carbon atom), 121.5 (vinyl carbon atoms), 126.8 (vinyl carbon atoms), 179.2 (carbonyl carbon

atom); IR (cm^{-1} , thin film), 3040 (m, broad) (carboxyl O–H str), 1707 (s) ($\text{C}=\text{O}$ str); mass spectrum (m/e , % of base), 79 (100), 124 (M^+ , 13).

2.5.2. 2,5-Cyclohexadienecarbonyl chloride

Into a dry, 250 ml, three-necked, round-bottomed flask fitted with a magnetic stirring bar, a Liebig condenser bearing a gas-inlet tube, a pressure-equilizing dropping funnel, and a gas-outlet tube connected to a water trap was placed 5.01 g (40.4 mmol) of 2,5-cyclohexadienecarboxylic acid and one drop of *N,N*-dimethylformamide (DMF). The mixture was stirred as 7.14 g (60.0 mmol) of thionyl chloride was added dropwise over a period of 0.5 h. After the addition was complete, the mixture was stirred at room temperature until gas evolution ceased (approximately 3 h). Excess thionyl chloride was removed by evaporation at reduced pressure to afford 2,5-cyclohexadienecarbonyl chloride as a pale yellow liquid: ^1H NMR (δ , CDCl_3) 2.74 (m, 2H, methylene protons), 4.16 (m, 1H, methine proton), 5.89 (m, 2H, vinyl protons), 6.02 (m, 2H, vinyl protons); ^{13}C NMR (δ , CDCl_3) 26.0 (methylene carbon atom), 52.0 (methine carbon atom), 120.1 (vinyl carbon atoms), 173.6 (carbonyl carbon atom); IR (cm^{-1} , thin film), 3042 (s) ($\text{C}_{\text{sp}^2}\text{-H}$ str), 2880 and 2817 (m) ($\text{C}_{\text{sp}^3}\text{-H}$ str), 1788 (s) ($\text{C}=\text{O}$ str of acyl chloride).

2.5.3. Ethyl 2,5-cyclohexadienecarboxylate

Into a dry, 250 ml, three-necked, round-bottomed flask fitted with a magnetic stirring bar, an Allihn condenser bearing a gas-inlet tube, and a pressure-equilizing dropping funnel was placed 1.01 g (0.021 mol) of anhydrous ethanol, 2.02 g (0.020 mol) of triethylamine and 30 ml of anhydrous diethyl ether. The solution was cooled to near 0 °C (external ice bath) and stirred under a static atmosphere of dry nitrogen as a solution of 2.01 g (0.014 mol) of 2,5-cyclohexadienecarbonyl chloride in 10 ml of anhydrous diethyl ether was added dropwise over a period of 0.5 h. After the addition was complete, the mixture was allowed to stir at room temperature for 3.0 h and poured into 200 ml of water. The resulting aqueous mixture was extracted with three 50-ml portions of diethyl ether. The ether extracts were combined, washed with 50 ml of saturated aqueous sodium chloride solution and dried over anhydrous sodium sulfate. The solvent was removed from the ether solution by rotary evaporation

at reduced pressure. The residue was purified by column chromatography (silica gel, 60–100 mesh; hexane/ethyl acetate, 10:1, as eluant) to provide the ester (1.56 g, 73.7% yield) as a colorless liquid: ^1H NMR (δ , CDCl_3) 1.27 (t, $J = 7.2$ Hz, 3H, methyl protons of ethyl group), 2.66 (m, 2H, cyclohexyl methylene protons), 3.72 (m, 1H, cyclohexyl methine proton), 4.16 (q, $J = 7.2$ Hz, 2H, methylene protons of ethyl group), 5.84 (m, 2H, vinyl protons), 5.87 (m, 2H, vinyl protons); ^{13}C NMR (δ , CDCl_3) 14.2 (methyl carbon atom), 25.8 (cyclohexyl methylene carbon atom), 41.7 (cyclohexyl methine carbon atom), 60.8 (methylene carbon atom adjacent to oxygen), 122.2 (vinyl carbon atoms), 126.3 (vinyl carbon atoms); IR (cm^{-1} , thin film), 3040 (w) ($\text{C}_{\text{sp}^2}\text{-H}$ str), 2981 and 2872 (m) ($\text{C}_{\text{sp}^3}\text{-H}$ str), 1736 (s) (C=O str), 1179 (m) (C-O str); mass spectrum (m/e , % of base), 79 (100), 107 (2), 123 (1), 137 (1), 152 (M^+ , 4).

Other alkyl 2,5-cyclohexadienecarboxylates were prepared using methods similar to that for the preparation of the ethyl ester.

2.5.4. Butyl 2,5-cyclohexadienecarboxylate

Butyl 2,5-cyclohexadienecarboxylate was purified by column chromatography (silica gel, 60–100 mesh; hexane/ethyl acetate, 30:1, as eluant) to provide the ester (1.67 g, 66.4% yield) as a colorless liquid: ^1H NMR (δ , CDCl_3) 0.98 (t, $J = 7.4$ Hz, 3H, methyl protons of butyl group), 1.37 (m, 2H, methylene protons), 1.63 (m, 2H, methylene protons), 2.71 (m, 2H, cyclohexyl methylene protons), 3.72 (m, 1H, cyclohexyl methine proton), 4.11 (t, $J = 6.8$ Hz, 2H, methylene protons of butyl group adjacent to oxygen), 5.83 (m, 2H, vinyl protons), 5.86 (m, 2H, vinyl protons); ^{13}C NMR (δ , CDCl_3) 14.2 (methyl carbon atom), 19.1 (methylene carbon atom), 25.8 (cyclohexyl methylene carbon atom), 30.6 (methylene carbon atom), 41.8 (cyclohexyl methine carbon atom), 64.8 (methylene carbon atom adjacent to oxygen), 122.2 (vinyl carbon atoms), 126.3 (vinyl carbon atoms); IR (cm^{-1} , thin film), 3040 (w) ($\text{C}_{\text{sp}^2}\text{-H}$ str), 2960 and 2874 (m) ($\text{C}_{\text{sp}^3}\text{-H}$ str), 1737 (s) (ester C=O str), 1177 (m) (C-O str); mass spectrum (m/e , % of base), 79 (100), 107 (3), 123 (2), 180 (M^+ , 4).

2.5.5. Hexyl 2,5-cyclohexadienecarboxylate

Hexyl 2,5-cyclohexadienecarboxylate was purified by column chromatography (silica gel, 60–100 mesh;

hexane/ethyl acetate, 40:1, as eluant) to provide the ester (1.97 g, 67.6% yield) as a colorless liquid: ^1H NMR (δ , CDCl_3) 0.90 (t, $J = 7.1$ Hz, 3H, methyl protons of hexyl group), 1.37 (m, 6H, methylene protons), 1.59 (m, 2H, methylene protons), 2.66 (m, 2H, cyclohexyl methylene protons), 3.71 (m, 1H, cyclohexyl methine proton), 4.10 (t, $J = 6.8$ Hz, 2H, methylene protons of hexyl group adjacent to oxygen), 5.79 (m, 2H, vinyl protons), 5.87 (m, 2H, vinyl protons); ^{13}C NMR (δ , CDCl_3) 14.0 (methyl carbon atom), 22.5 (methylene carbon atom), 25.8 (cyclohexyl methylene carbon atom), 25.5, 28.5, and 31.4 (methylene carbon atoms), 41.8 (cyclohexyl methine carbon atom), 65.1 (methylene carbon atom adjacent to oxygen), 122.2 (vinyl carbon atoms), 126.3 (vinyl carbon atoms), 172.7 (acyl carbon atom); IR (cm^{-1} , thin film), 3039 (w) ($\text{C}_{\text{sp}^2}\text{-H}$ str), 2931 and 2860 (m) ($\text{C}_{\text{sp}^3}\text{-H}$ str), 1737 (s) (ester C=O str), 1175 (m) (C-O str); mass spectrum (m/e , % of base), 79 (100), 107 (2), 123 (92), 208 (M^+ , 6).

2.5.6. Octyl 2,5-cyclohexadienecarboxylate

Octyl 2,5-cyclohexadienecarboxylate was purified by column chromatography (silica gel, 60–100 mesh; hexane/ethyl acetate, 50:1, as eluant) to provide the ester (2.10 g, 63.5% yield) as a colorless liquid: ^1H NMR (δ , CDCl_3) 0.87 (t, $J = 6.2$ Hz, 3H, methyl protons of octyl group), 1.30 (m, 10H, methylene protons), 1.64 (m, 2H, methylene protons), 2.70 (m, 2H, cyclohexyl methylene protons), 3.72 (m, 1H, cyclohexyl methine proton), 4.09 (t, $J = 6.6$ Hz, 2H, methylene protons of octyl group adjacent to oxygen), 5.84 (m, 2H, vinyl protons), 5.87 (m, 2H, vinyl protons); ^{13}C NMR (δ , CDCl_3) 14.1 (methyl carbon atom), 22.61 (methylene carbon atom), 25.8 (cyclohexyl methylene carbon atom), 25.83, 28.54, 29.14, 31.55, and 31.7 (methylene carbon atoms), 41.8 (cyclohexyl methine carbon atom), 65.1 (methylene carbon atom adjacent to oxygen), 122.2 (vinyl carbon atoms), 126.3 (vinyl carbon atoms), 172.0 (acyl carbon atom); IR (cm^{-1}), 3040 (w) ($\text{C}_{\text{sp}^2}\text{-H}$ str), 2928 and 2857 (m) ($\text{C}_{\text{sp}^3}\text{-H}$ str), 1738 (s) (ester C=O str), 1175 (m) (C-O str); mass spectrum (m/e , % of base), 79 (100) 107 (3), 123 (63), 236 (M^+ , 6).

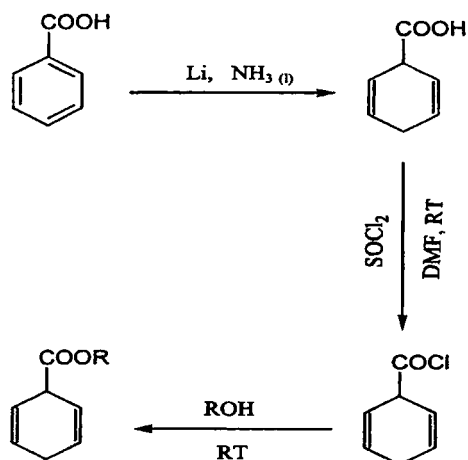
2.5.7. Dodecyl 2,5-cyclohexadienecarboxylate

Dodecyl 2,5-cyclohexadienecarboxylate was purified by column chromatography (silica gel, 60–100

mesh; hexane/ethyl acetate, 30:1, as eluant) to provide the ester (2.52 g, 61.3% yield) as a colorless liquid: ^1H NMR (δ , CDCl_3) 0.88 (t, $J = 6.6$ Hz, 3H, methyl protons of dodecyl group), 1.26 (m, 18H, methylene protons), 1.64 (m, 2H, methylene protons), 2.67 (m, 2H, cyclohexyl methylene protons), 3.72 (m, 1H, cyclohexyl methine proton), 4.10 (t, $J = 6.8$ Hz, 2H, methylene protons of dodecyl group adjacent to oxygen), 5.83 (m, 2H, vinyl protons), 5.87 (m, 2H, vinyl protons); ^{13}C NMR (δ , CDCl_3) 14.1 (methyl carbon atom), 22.7 (methylene carbon atom), 25.8 (cyclohexyl methylene carbon atom), 28.54, 29.19, 29.31, 29.47, 29.53, 29.60, 29.61, and 31.88 (methylene carbon atoms), 41.8 (cyclohexyl methine carbon atom), 65.1 (methylene carbon atom adjacent to oxygen), 122.2 (vinyl carbon atoms), 126.3 (vinyl carbon atoms), 172.7 (acyl carbon atom); IR (cm^{-1} , thin film), 3039 ($\text{C}_{\text{sp}^2}\text{-H}$ str), 2925 and 2854 (s) ($\text{C}_{\text{sp}^3}\text{-H}$ str), 1739 (s) (ester $\text{C}=\text{O}$ str), 1175 (m) ($\text{C}-\text{O}$ str); mass spectrum (m/e , % of base), 79 (100), 107 (2), 123 (4), 292 (M^+ , 2).

3. Results and discussion

VDC polymers are extremely important materials for food packaging. As noted previously these polymers exhibit high barrier to the transport of oxygen (to prevent spoilage of food items stored in packages containing these polymers as functional components) as well as to the transport of flavor and aroma constituents (to prevent scalping, or loss of flavor and taste while sitting on the supermarket or warehouse shelf). Thus these materials have come to occupy a place of prominence in the barrier plastic packaging industry. While these polymers exhibit extremely useful properties they must be processed with care and in the presence of stabilizing additives to avoid severe degradative dehydrochlorination. Substituted 1,4-cyclohexadienes might serve as useful stabilizers for these polymers. They are known to be good hydrogen atom transfer agents and if the substituent is selected properly they would be compatible with food packaging applications. Accordingly, 2,5-cyclohexadienecarboxylic acid and a series of alkyl esters have been synthesized and examined as potential stabilizers for a standard VDC/methyl acrylate (9 wt.%) copolymer.

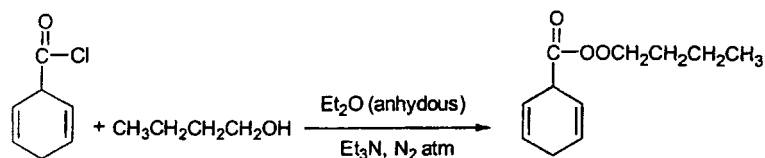


Scheme 1. Synthesis of 2,5-cyclohexadienecarboxylates.

The synthesis of the alkyl 2,5-cyclohexadienecarboxylates was based on benzoic acid as an inexpensive starting material and are outlined in Scheme 1. Dissolving metal reduction of benzoic acid provided 2,5-cyclohexadienecarboxylic acid in excellent (>90%) yield [10]. NMR spectral data for this compound are displayed in Table 1. The carboxylic acid could readily be converted to the corresponding acid chloride by treatment with thionyl chloride in the presence of a catalytic amount of DMF. Both proton and carbon NMR spectral data for this compound are summarized in Table 2. Treatment of an ether solution of any of various alcohols (ethyl, butyl, hexyl, octyl, dodecyl) containing triethylamine with 2,5-cyclohexadienecarbonyl chloride afforded the corresponding ester in good yield (60–75%). This is illustrated in Scheme 2 for the preparation of the butyl ester. The crude ester in each case was purified by column

Table 1
 ^1H and ^{13}C NMR spectral data for 2,5-cyclohexadienecarboxylic acid

Carbon or proton label	δ (proton)	δ (carbon)	Structure
1	2.70 (m)	25.8	
2	3.78 (m)	41.5	
3	5.83 (m)	121.5	
4	5.9 (m)	126.8	
5	10.97 (s, br)	179.2	



Scheme 2. Synthesis of butyl 2,5-cyclohexadienecarboxylate.

Table 2
¹H and ¹³C NMR spectral data for 2,5-cyclohexadienecarbonyl chloride

Carbon or proton label	δ (proton)	δ (carbon)	Structure
1	2.74 (m)	26.0	
2	4.16 (m)	53.0	
3	5.89 (m)	121.1	
4	6.02 (m)	128.8	
5		173.6	

chromatography (silica gel; hexane/ethyl acetate as eluant). Spectral parameters for the esters are shown in Tables 3 and 4. 2,5-Cyclohexadienecarboxylic acid and the corresponding ethyl ester were selected for initial stabilization studies. Blends (1, 5 and 10 wt.%) of these compounds with a standard VDC/methyl acrylate (9 wt.%) copolymer were prepared and subjected to examination by thermogravimetry. Thermograms for the degradation of blends of 2,5-cyclohexadienecarboxylic acid with the polymer are shown in Fig. 1. A qualitative comparison of the various thermograms suggested that the presence of

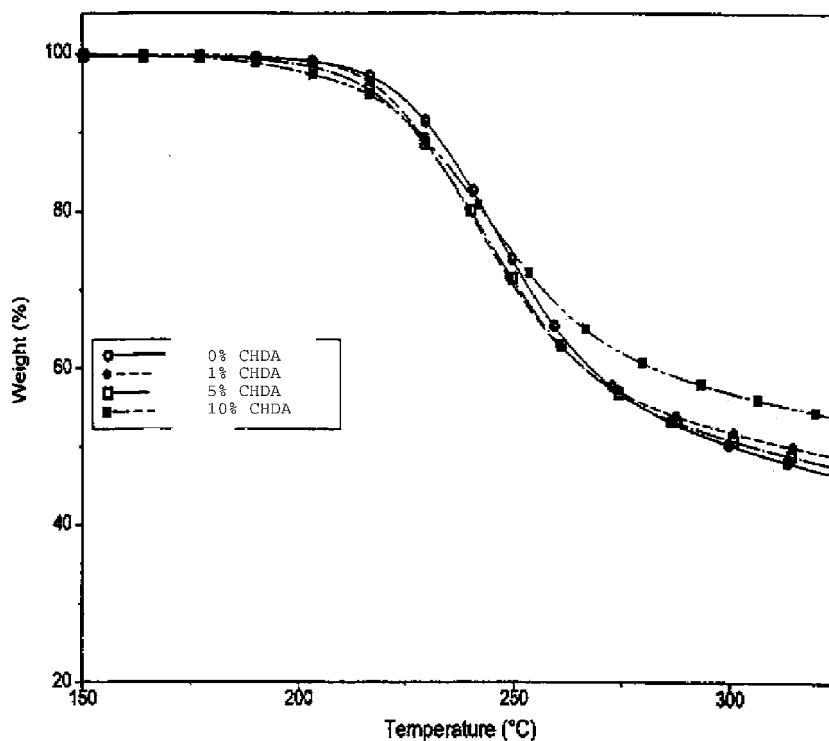


Fig. 1. Thermal decomposition of a VDC/methyl acrylate (9 wt.%) copolymer blended with varying amounts of 2,5-cyclohexadienecarboxylic acid.

Table 3
 ^1H and ^{13}C NMR spectral data for alkyl 2,5-cyclohexadienecarboxylates

Alkyl group	δ (proton)	δ (carbon)
Ethyl	1.27 (t, $J = 7.2$ Hz), 2.66 (m), 3.72 (m), 4.16 (q, $J = 7.2$ Hz)	14.2, 25.8, 41.7, 60.8, 122.2, 126.3, 172.6
Butyl	0.98 (t, $J = 7.4$ Hz), 1.37 (m), 1.63 (m), 2.71 (m), 3.72 (m), 4.11 (t, $J = 6.8$ Hz), 5.83 (m), 5.86 (m)	13.7, 19.1, 25.8, 30.6, 41.8, 64.8, 122.2, 126.3, 172.6
Hexyl	0.90 (t, $J = 7.1$ Hz), 1.37 (m), 1.59 (m), 2.66 (m), 3.71 (m), 4.10 (t, $J = 6.8$ Hz), 5.83 (m), 5.86 (m)	14.0, 22.5, 25.5, 5.8, 28.5, 31.4, 41.8, 64.8, 122.2, 126.3, 172.7
Octyl	0.87 (t, $J = 6.2$ Hz), 1.30 (m), 1.64 (m), 2.70 (m), 3.72 (m), 4.09 (t, $J = 6.6$ Hz), 5.83, 5.87	14.1, 22.6, 25.80, 25.83, 28.5, 29.1, 31.6, 31.7, 41.8, 65.1, 122.2, 126.3, 172.7
Dodecyl	0.88 (t, $J = 6.6$ Hz), 1.26 (m), 1.64 (m), 2.67 (m), 3.72 (m), 4.10 (t, $J = 6.8$ Hz), 5.83, 5.87	14.1, 22.7, 25.80, 25.83, 28.5, 29.2, 29.3, 29.47, 29.53, 29.60, 29.61, 31.9, 41.8, 65.1, 122.2, 126.3, 172.7

Table 4
Infrared and mass spectral features for alkyl 2,5-cyclohexadienecarboxylates

Alkyl group	Infrared (cm ⁻¹) (intensity)	MS <i>m/e</i> (% of base)
Ethyl	3040 (w), 2981 (m), 2872 (m), 1736 (s), 1179 (m)	79 (100), 107 (2), 123 (1), 152 (<i>M</i> ⁺ , 4)
Butyl	3040 (w), 2960 (m), 2874 (m), 1737 (s), 1177 (m)	79 (100), 107 (3), 123 (2), 180 (<i>M</i> ⁺ , 4)
Hexyl	3039 (w), 2931 (m), 2860 (m), 1737 (s), 1175 (m)	79 (100), 107 (2), 123 (92), 208 (<i>M</i> ⁺ , 6)
Octyl	3040 (w), 2928 (m), 2857 (m), 1738 (s), 1175 (m)	79 (100), 107 (3), 123 (63), 236 (<i>M</i> ⁺ , 6)
Dodecyl	3039 (m), 2925 (s), 2854 (s), 1739 (s), 1175 (m)	79 (100), 107 (2), 123 (4), 292 (<i>M</i> ⁺ , 2)

Table 5
Onset temperature and temperature of maximum degradation rate for a VDC/methyl acrylate (9 wt.%) copolymer blended with varying amounts of 2,5-cyclohexadienecarboxylic acid

2,5-Cyclohexadienecarboxylic acid (wt.%)	Extrapolated onset temperature for degradation (°C) ^a	Temperature for maximum degradation rate (°C) ^b
0	209	246
1	205	240
5	203	243
10	202	244

^a From the derivative plot of weight loss versus temperature.

^b Maximum in the derivative plot of weight loss versus temperature.

Table 6
Rate constants for thermal degradation at 180 °C of a VDC/methyl acrylate (9 wt.%) copolymer in the presence of 2,5-cyclohexadienecarboxylic acid

2,5-Cyclohexadienecarboxylic acid (wt.%)	<i>k</i> _i (×10 ⁻⁵ s ⁻¹) ^a	<i>k</i> _p (×10 ⁻⁵ s ⁻¹) ^a
0	2.48 ± 0.03	4.11 ± 0.04
1	7.50 ± 0.49	9.14 ± 0.50
5	10.18 ± 2.43	10.54 ± 2.86
10	9.35 ± 1.34	9.28 ± 1.83

^a Averages of two determinations.

the additive has little impact on the thermally induced degradation of the polymer. The temperatures for the onset of degradation are shown in Table 5 which supports this observation. In fact, the onset temperature for degradation actually decreases modestly as the level of additive is increased. A more quantita-

tive reflection of the impact of the presence of the additive on the stability of the polymer is provided by the rate constants presented in Table 6. Both the rate constants for the initiation of degradation and its propagation increase with increasing level of additive present. While these increases are not large, it is clear

Table 7
Rate constants for thermal degradation at 180 °C of a VDC/methyl acrylate (9 wt.%) copolymer in the presence of ethyl 2,5-cyclohexadienecarboxylate

Ethyl 2,5-Cyclohexadienecarboxylate (wt.%)	<i>k</i> _i (×10 ⁻⁵ s ⁻¹) ^a	<i>k</i> _p (×10 ⁻⁵ s ⁻¹) ^a
0	2.48 ± 0.03	4.11 ± 0.04
1	8.81 ± 1.03	9.34 ± 0.83
4	11.54 ± 0.06	9.59 ± 0.31
5	11.85 ± 0.12	9.32 ± 0.25

^a Averages of two determinations.

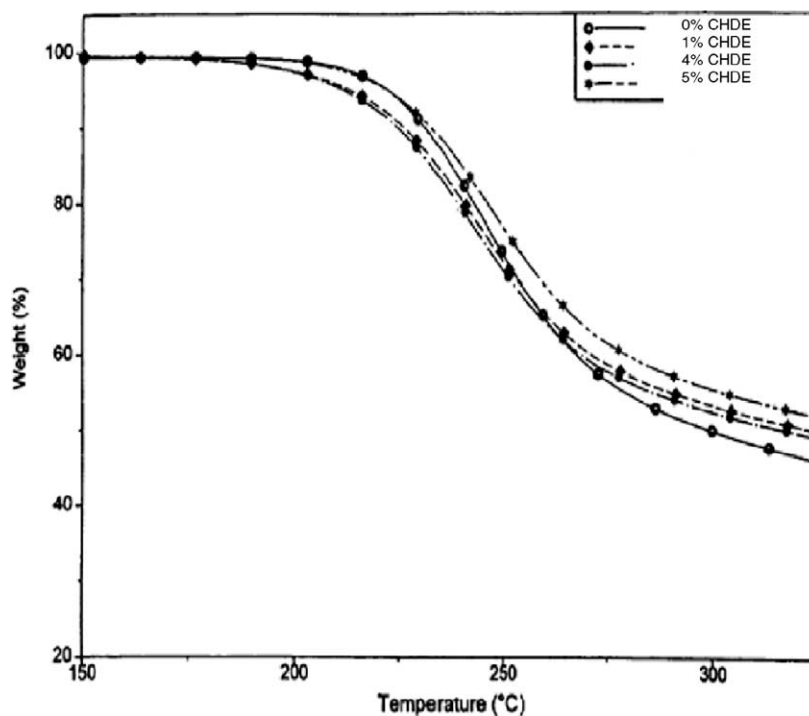


Fig. 2. Thermal degradation of a VDC/methyl acrylate (9 wt.%) copolymer blended with varying amounts of ethyl 2,5-cyclohexadienecarboxylate.

that the presence of the carboxylic acid does not have a stabilizing influence on the polymer. Results obtained using the ethyl ester as additive were no more positive. As may be seen in Fig. 2 varying levels of ethyl 2,5-cyclohexadienecarboxylate have little impact on the degradation characteristics of the polymer. Rate constants for degradation of the polymer/ester blends are shown in Table 7. As can be seen, the presence of the ester has a small but negative effect on the stability of the polymer. The initiation rate constants

increase slightly with increasing amounts of ester in the blend. The impact of the presence of the ester on the rate constant for propagation of degradation is smaller but in the same direction as that for the initiation rate constants obtained for the degradation of the polymer/ester blends. The rate constants are consistent with the qualitative reflection of degradation behavior is shown in Fig. 2.

The onset temperatures for degradation of these blends (Table 8) are also consistent with these obser-

Table 8

Onset temperature and temperature of maximum degradation rate for a VDC/methyl acrylate (9 wt.%) copolymer blended with varying amounts of ethyl 2,5-cyclohexadienecarboxylate

Ethyl 2,5-cyclohexadienecarboxylate (wt.%)	Extrapolated onset temperature for degradation (°C) ^a	Temperature for maximum degradation rate (°C) ^b
0	209	246
1	207	247
4	205	244
5	205	243

^a From the derivative plot of weight loss versus temperature.

^b Maximum in the derivative plot of weight loss versus temperature.

Table 9

Rate constants for thermal degradation at 180 °C of a VDC/methyl acrylate (9 wt.%) copolymer pretreated with a solution of 2,5-cyclohexadienecarboxylic acid (2 moles per mole of VDC units) in chlorobenzene at 130 °C for 2 h

Pretreatment	k_i ($\times 10^{-5} \text{ s}^{-1}$) ^a	k_p ($\times 10^{-5} \text{ s}^{-1}$) ^a
None	2.48 ± 0.03	4.11 ± 0.04
2,5-Cyclohexadienecarboxylic acid	9.75 ± 0.13	6.72 ± 0.62

^a Averages of two determinations.

Table 10

Onset temperature and temperature of maximum degradation rate for a VDC/methyl acrylate (9 wt.%) copolymer pretreated with a solution of 2,5-cyclohexadienecarboxylic acid (2 moles per mole of VDC units) in chlorobenzene at 130 °C for 2 h

Additive	Extrapolated onset temperature for degradation (°C) ^a	Temperature for maximum degradation rate (°C) ^b
None	209	246
2,5-Cyclohexadienecarboxylic acid	208	247

^a From the derivative plot of weight loss versus temperature.

^b Maximum in the derivative plot of weight loss versus temperature.

vations. They tend to decrease slightly with increasing levels of dienecarboxylate in the blend. All the data for the blends of a typical VDC polymer with 1,4-cyclohexadiene derivatives, either carboxylic acid or ester, suggest that the presence of the diene has little impact on the stability of the polymer. This is probably reflective of the inaccessibility of the components of the radical pair formed in the degradation of the polymer. It is known that the carbon–chlorine atom radical pair formed from homolysis of a carbon–chlorine bond of a VDC unit of polymers of this kind does not dissociate readily [6]. Therefore, trapping of either component of the radical pair is not very efficient with a variety of good trapping agents [11].

To determine whether or not more intimate contact between the polymer and diene might enhance the stabilizing influence of the diene, a solution of the polymer and 2,5-cyclohexadienecarboxylic acid (2 moles per mole of VDC units in the polymer) in chlorobenzene was stirred for 2 h at 130 °C. The polymer was then isolated, dried, and examined by thermogravimetry. As a control, a portion of the polymer was subjected to the same treatment in absence of the dienecarboxylic acid. Rate constants for the thermal degradation of these materials are shown in Table 9. While there is a minimal difference between the rate constants for degradation of the treated versus the untreated polymer, the treated polymer is some-

what more prone to degradation than the untreated control. The temperature for the onset of degradation (Table 10) is identical for the two polymers. Thus by any measure, pretreatment of the polymer with a 1,4-cyclohexadiene derivative had no impact on the stability of the polymer.

4. Conclusions

Although compounds containing the 1,4-cyclohexadiene structure are good hydrogen transfer agents, neither 2,5-cyclohexadienecarboxylic acid nor its alkyl esters, present as surface blends, are effective stabilizers for VDC polymers. This is probably reflective of the inaccessibility of the allylic carbon, chlorine atom radical pair responsible for propagation of the degradation reaction.

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