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DETERMINATION OF THE PRINCIPAL DEFECT SITE RESPONSIBLE FOR SARAN DEGRADATION USING THERMOGRAVIMETRIC ANALYSIS

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ABSTRACT

Three sets of Saran polymers, i.e., copolymers which contain vinylidene chloride (VDC) as a major component, have been examined using thermogravimetric (TGA) methods. The first was a series of copolymers of vinylidene chloride and small but varying amounts of phenylacetylene (0.05-5%) to introduce measurable and quantifiable amounts of unsaturation. The second was a typical Saran copolymer containing 9% methyl acrylate and again small amounts of phenylacetylene. The third was a set of vinylidene chloride/methyl acrylate (VDC/MA) copolymers containing no phenylacetylene. The degradation reaction is a typical chain process involving distinct initiation, propagation and termination phases. The incorporation of unsaturation into the polymer backbone has little effect on the rate of the propagation reaction (propagation rate constants are essentially constant independent of the level of phenylacetylene loading) but dramatically enhances the rate of initiation. In contrast, degradation initiation rates for VDC/MA copolymers containing no phenylacetylene are constant over a broad range (2-20%) of MA content. Thus the double bond has been established as a prominent defect site responsible for Saran degradation. The impact of an increasing number of such defect sites is to enhance the initiation rate for degradative dehydrochlorination.

INTRODUCTION

Copolymers which contain vinylidene chloride (VDC) as a major component have a number of superior characteristics including high crystallinity and outstanding resistance to nonbasic solvents and reagents.[1,2] However, the unique feature which sets these materials apart from most other vinyl polymers is their extremely low permeability to a wide variety of gases, most notably oxygen and water.[3] This has led to the widespread use of these polymers as barrier materials in food packaging applications.[4] Copolymers of vinylidene chloride with alkyl acrylates are particularly suitable for such use. These copolymers are typically less crystalline, more soluble, lower melting, and subject to a greater ease of processing than is the VDC homopolymer. In particular, the copolymers suffer far less degradative damage during processing than does the homopolymer.[5] Most evidence suggests that these polymers are regular, head-to-tail, unbranched, and highly crystalline. The defect structures common to many vinyl polymers, e.g., poly(vinyl chloride) are absent.[6-10] It might, therefore, be anticipated

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that internal double bonds introduced during the preparation and/or processing of these polymers are the sites responsible for the initiation of degradation. To determine the role of internal unsaturation in inducing degradative dehydrochlorination in these materials, three sets of copolymers which contain VDC as a major component have been prepared and examined using thermogravimetric (TGA) methods. The first was a series of vinylidene chloride/phenylacetylene (VDC/PA) copolymers containing small but varying amounts of phenylacetylene (to introduce a known concentration of unsaturation sites along the polymer chain), the second was a series of vinylidene chloride/methyl acrylate/phenylacetylene (VDC/MA/PA) terpolymers containing a constant nine weight percent methyl acrylate and small but varying amounts of phenylacetylene, and the third was a series of vinylidene chloride/methyl acrylate (VDC/MA) copolymers containing 0,2,5,9,12 and 20 weight percent methyl acrylate.

EXPERIMENTATION

Synthesis

The VDC copolymers were prepared by suspension polymerization carried out to high conversion in glass vessels (Bendix polymerizer at 65°). The aqueous phase contained 0.2 weight percent hydroxymethylcellulose as suspending agent. Initiator (AIBN; 0.3 mol%) was dissolved in the monomer phase. A phase ratio of 1.5:1 (mass water to mass monomer) was maintained.

Characterization

Molecular Weight Determination

Molecular weights were determined by size-exclusion chromatography relative to polystyrene standards. For the VDC/PA copolymers $\bar{M}_w$ was 55-80,000 with a dispersity of 1.9-2.4 (for the polymer containing 5% PA, $\bar{M}_w$ was lower: 18,500). The weight average molecular weights for all the VDC/MA/PA terpolymers were within the range 85,000-120,000 with $\bar{M}_w/\bar{M}_n$ of 2.03-2.35. Similar values for the VDC/MA copolymers were within the range 82,000-120,000 with $\bar{M}_w/\bar{M}_n$ of 2.24-2.39.

Differential Scanning Calorimetry (DSC)

Analysis by DSC was accomplished using a DuPont 9900-912 DSC unit. In general, 10-15 mg samples and aluminum sample pans were used. The cell was subject to a constant nitrogen purge. After equilibration at -40°C, the temperature was ramped at 10°C/min. to 210°C. Often, in an attempt to observe a sharp glass transition temperature (T_g) and/or a crystallization exotherm (T_c) the melted sample was rapidly cooled to -40°C and the run repeated.[11,12] Alternatively, fresh samples were annealed 75 s at 180-200°C, quenched in liquid nitrogen and placed in the DSC cell at -40°C, and a standard scan was recorded.

All the samples displayed a characteristic premelt endotherm about 25°C below the melting endotherm.[11,12] The area of the premelt endotherm (T_{pm}) in the DSC scans of the untreated polymers was generally 10-15% of the area for the melting endotherm. For samples which had been melted and then quenched at low temperature before being subjected to DSC analysis, the premelt temperature was much closer to the melting temperature, i.e., the premelt endotherm had moved toward the melting endotherm—in some cases these coincided so that a single melting endotherm was observed for these samples. Temperatures for the thermal transitions in the VDC/PA copolymers are listed in Table 1.

Table 1. Thermal Transitions for Vinylidene Chloride/Phenylacetylene (VDC/PA) Copolymers

Wt% PA	T_g (°C)	T_c (°C)	T_{pm} (°C)	T_m (°C)
0.0	-3.6		174.7	201.5
0.05	-2.9		174.0	200.6
0.1	-6.7		174.6	201.4
0.3	2.9	52.4	172.1	198.9
0.5	-3.7	57.4	172.0	198.6
1.0	-4.0	57.3	171.4	193.0
5.0	-2.2			

For the series of terpolymers containing a constant nine weight percent methyl acrylate as well as PA and a balance of VDC, melting endotherms were usually preceded by a premelt that extended over a range of several degrees. This premelt tailed into the main T_m peak rather than appearing as a distinct second peak as was observed for the VDC/PA copolymers.[13] Values for both T_g and T_m for this series are listed in Table 2.

Table 2. Thermal Transitions for VDC/MA/PA Terpolymers

Wt% PA	T_g (°C)	T_m (°C)
0.0	20.8	148.5
0.05	20.5	151.7
0.10	20.1	147.9
0.20	18.6	150.7
0.30	18.9	149.0
0.40	18.6	148.6

Thermal transitions for the series of VDC/MA copolymers are listed in Table 3. As the MA content increased, the glass transition (T_g) for the polymer also increased.[2,5] For the low MA content copolymers melting endotherms (T_m) were preceded by distinct premelt peaks (T_{pm}). For high MA content (5-20%) copolymers, a sharp T_{pm} peak was not observed. Instead the premelt extended over a range of several degrees preceding and tailing into the main T_m peak. The observed T_m was also dependent upon the level of MA in the polymer; as the MA content increased, T_m for the copolymer decreased.

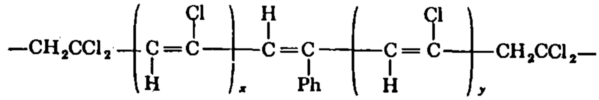
Table 3. Thermal Transitions for VDC/MA Copolymers

Wt% MA	T_g (°C)	T_c (°C)	T_{pm} (°C)	T_m (°C)
0.0	-3.6		175.5	202.2
2.0	0.7	50.2	170.6	190.6
5.0	12.5			164.0
9.0	20.8			148.5
20.0	30.6			122.0

Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra, both proton and carbon, were recorded using solutions in the THF-d_8 or DMF-d_7 and a Nicolet NT-300 spectrometer. Carbon spectra were observed at 75.46 MHz with a pulse width of 18 μs (90°), a pulse depth of 10 s, an acquisition time of 0.41 s, gated decoupling without NOE, a sweep width of 20 kHz, and an acquisition size of 16 K.

For all copolymers the nmr analysis established that both phenylacetylene and methyl acrylate were randomly incorporated into the polymer and that the comonomers were incorporated at approximately the distributions in the initial monomer mixture.[5,14,15] In addition, it demonstrated that for the VDC/PA copolymers each phenylacetylene unit was contained within a polyene block of 7-8 units, i.e., the incorporation of phenylacetylene into the growing polymer chain had induced dehydrochlorination during the polymerization process such that structures of the following type had been formed.[16]



$$-CH_2CCl_2-\left(\underset{H}{C}=\overset{Cl}{C}\right)_x-\overset{H}{C}=\underset{Ph}{C}-\left(\underset{H}{C}=\overset{Cl}{C}\right)_y-CH_2CCl_2-$$

Similar polyene blocks were also present in the VDC/MA/PA terpolymers except that the block length was somewhat shorter: 3-7 units.[13] In both cases the number of polyene segments was equivalent to the amount of phenylacetylene incorporated, i.e., the number of unsaturation sites was directly reflected by the phenylacetylene incorporation.

Degradation

Thermal degradation of the copolymers was examined by thermogravimetric analysis (TGA) using a DuPont model 951 TGA unit coupled to the appropriate data handling accessories. The TGA cell was swept with a nitrogen flow, 25 ml/min., during degradation runs, and the sample, approximately 30 mg, was contained in a platinum sample pan. To study decomposition propagation, samples were brought to 188°C (10 min were required for temperature equilibration) and weight loss was monitored as a function of time for at least two half-lives. For each sample at least one run was carried-out to 10 half-lives to assure that the degradation was well-behaved to completion. Under these conditions, the clean, first-order loss of mass corresponding to ca. 1 mol of hydrogen chloride was observed in every case. Temperature control was ±0.2°C. Rate constants were determined from the slope of a plot of

$$\ln\left(\frac{W_\infty - W_0}{W_\infty - W_t}\right) \text{ versus time}$$

where W_∞ is the weight of the sample at infinite time (t_∞) taken as that weight which would remain after 37.62% of the initial vinylidene chloride component weight (corresponding to the complete loss of 1 mol of hydrogen chloride per vinylidene chloride unit in the copolymer) has been lost; W_0 is the weight at time zero (t_0), i.e., the time at which the first data point was recorded (weight loss during the time allowed for temperature equilibration varied from less than 2% of the initial weight for polymers containing no phenylacetylene to 28% for the sample containing 5% phenylacetylene and is reflective of the different rates of initiation); and W_t is the weight at any time, t, during the run. The values reported correspond to the linear, least-squares, best fit of the data. In all cases excellent first-order behavior was observed.

To assess the impact of internal unsaturation on the rate of initiation of degradation, weight loss as a function of temperature was also examined. In a typical run, the temperature was ramped from 50 to 280°C at 5°C/min.

RESULTS AND DISCUSSION

The degradation of poly(vinylidene chloride and copolymers occurs in two distinct steps. The first involves degradative dehydrochlorination via a chain process to generate poly(chloroacetylene) sequences.[13,16] Subsequent Diels-Alder type condensation between conjugated sequences affords a highly crosslinked network which on further dehydrochlorination leads to the formation of a large surface area, highly absorptive carbon.[2] The initial dehydrochlorination occurs at moderate temperatures (<200°C) and is a typical chain process involving distinct initiation, propagation, and termination phases.[17,18] Initiation is thought to occur via carbon-chlorine bond scission promoted by a defect structure within the polymer. An effective and probable defect site in these polymers is unsaturation. Introduction of a random double bond produces an allylic dichloromethylene unit activated for carbon-chlorine bond scission. Initiation by the thermally-induced cleavage of this bond followed by propagation by successive dehydrochlorination along the chain (the so called "zip" reaction) can then proceed readily. Rate constants for propagation of degradative dehydrochlorination for VDC/PA copolymers containing small but increasing amounts of unsaturation (induced by the presence of phenylacetylene in the polymer) are displayed in Table 4.

Table 4. Rate Constants for the Degradation of Vinylidene Chloride/Phenylacetylene (VDC/PA) Copolymers at 188°C

Polymer	Phenylacetylene content (%)	$k \times 10^4$ (s^{-1}) [a]
1	0.0	2.01 ± 0.17
2	0.05	2.27 ± 0.15
3	0.1	2.44 ± 0.30
4	0.3	2.54 ± 0.38
5	0.5	2.74 ± 0.33
6	1.0	2.87 ± 0.17
7	5.0	2.94 ± 0.22

[a] Averages of values from duplicate, triplicate, or multiple runs.

From examination of the data shown in Table 4 it is apparent that the rate constant for the propagation of dehydrochlorination is little affected by the level of phenylacetylene loading, i.e., the level of unsaturation within the polymer. In contrast, the presence of unsaturation dramatically impacts the rate of initiation for the dehydrochlorination reaction.

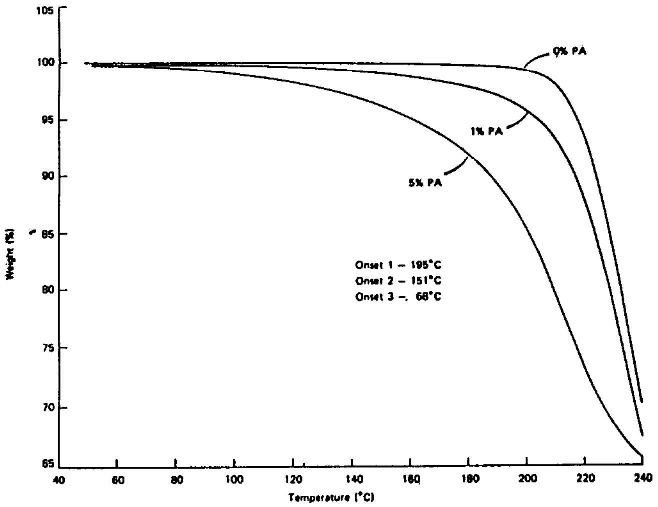


Figure 1. Weight loss for vinylidene chloride/phenylacetylene (VDC/PA) copolymers as a function of temperature: Impact of the presence of unsaturation on the initiation of degradative dehydrochlorination.

The data displayed in Figure 1 emphasize this observation and further indicate that with higher levels of unsaturation, the temperature at which degradation becomes prominent is lower. As evidenced by the point at which the plots (weight loss versus temperature) change slope (195°C for 0% PA, 151°C for 1% PA, 68°C for 5% PA), the onset of degradation is substantially earlier for copolymers containing higher levels of phenylacetylene. Further, as can be seen from the initial slopes of these plots, the rate of initiation increases markedly with increasing phenylacetylene content. As initiation is complete and propagation becomes the dominant process the slopes of the plots become quite similar.

Similar results were obtained for the degradation of the VDC/MA/PA terpolymers.

Table 5. Rate Constants for the Degradation of VDC/MA/PA Terpolymers at 188°C

Polymer	Percent PA	$k \times 10^4$ (s^{-1}) [a]
1	0.0	1.41 ± 0.07
2	0.05	1.38 ± 0.21
3	0.1	1.35 ± 0.10
4	0.2	1.39 ± 0.03
5	0.3	1.58 ± 0.15
6	0.4	1.62 ± 0.07
7	1.0	2.62 ± 0.02

[a] Average of values from duplicate runs.

As can be seen the rate constants for the propagation of dehydrochlorination (Table 5) are largely independent of the amount of internal unsaturation, i.e., phenylacetylene loading, contained within these polymers. This is in sharp contrast to the impact of such unsaturation on the rate of initiation of the degradation reaction.

The impact of unsaturation on the two stages of the reaction is clearly illustrated in Figure 2.

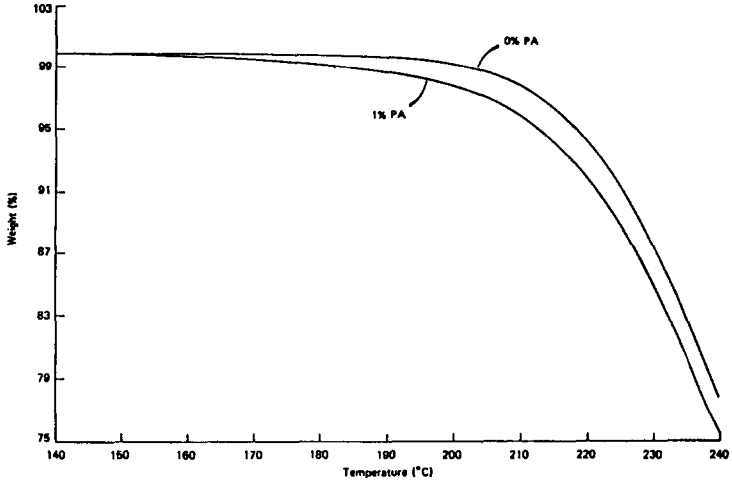


Figure 2. Thermal degradation of VDC/MA/PA terpolymers as a function of temperature.

In this case, weight loss is plotted as a function of temperature for the polymers containing zero and 1% phenylacetylene. It can readily be seen that the slopes of these plots are very different during the initiation stage of the dehydrochlorination reaction but become quite similar as initiation is completed and propagation becomes the dominant process. This behavior stands in sharp contrast to that of VDC/MA copolymers containing no phenylacetylene. As can be seen in Figure 3, the rates of initiation (and the point of the onset of degradation) of degradative dehydrochlorination are essentially identical for all of these polymers.

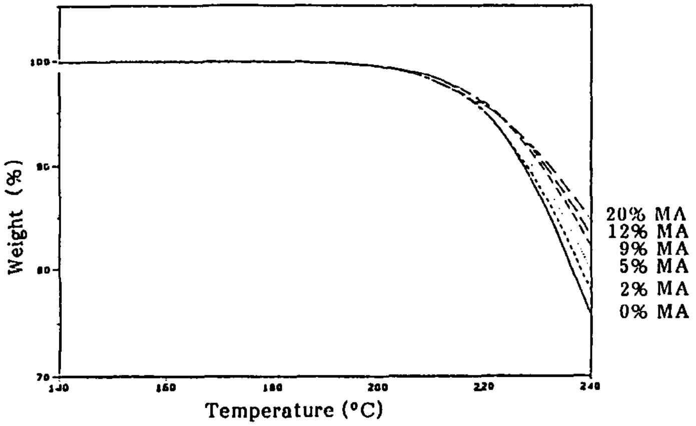


Figure 3. Weight loss for vinylidene chloride/methyl acrylate (VDC/MA) copolymers as a function of temperature: impact of methyl acrylate incorporation on the initiation of degradative dehydrochlorination.

Initiation rates for degradation might be expected to be very similar independent of the MA content of the copolymer since initiation occurs in VDC sequences and therefore is identical to the corresponding process for the homopolymer, PVDC. Propagation slopes for the degradation of the copolymers are smaller than that for the homopolymer and decrease in orderly fashion with increasing methyl acrylate content. This is consistent with the rate constants reported in Table 6 and with what might be expected.

Table 6. Propagation Rate Constants for the Degradation of VDC/MA Copolymers at 188°C.

Polymer	MA (wt.%)	$k \times 10^4$ (s^{-1}) [a]
1	0.0	2.01
2	2.0	1.63
3	5.0	1.57
4	9.0	1.41
5	12.0	1.40
6	20.0	1.36

[a] Average values from duplicate runs; average deviation < 0.2.

Since chain-stopping, i.e., termination, becomes more prominent as the size of VDC sequence becomes shorter, apparent propagation rates should decrease somewhat as the methyl acrylate content of the copolymers increases. In contrast to the case for PVDC degradation, the polyene sequences are limited in size by the level of acrylate incorporation, i.e., the acrylate molecules act as "stopper" units for the "unzipping" dehydrochlorination reaction. The impact of this chain-stopping is that the termination rate for higher methyl acrylate content polymers is greater than for those containing smaller amounts of methyl acrylate, i.e., initiation and termination rates are in balance for a shorter portion of the overall reaction period. The observed consequence of this is an apparent, albeit small, decrease in propagation rate with increasing methyl acrylate content of the polymer.

CONCLUSIONS

The presence of unsaturation in VDC polymers greatly facilitates degradative dehydrochlorination by enhancing the rate of initiation of the degradation reaction, i.e., by providing defect sites at which initiation can occur. Thus random double bonds introduced in a variety of ways (interaction of the polymer with heat, light, basic solvents, metal ions or other agents) may be identified as the principal defect structure responsible for the thermal instability of these materials.

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