

Heat and Ultraviolet Aging of Poly(vinyl chloride)¹

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Four poly(vinyl chloride) polymers prepared with different initiators were exposed to ultraviolet radiant energy and to heat, in a vacuum and in air. The gaseous products evolved were analyzed by mass spectrometry. Changes in chemical structure were followed by infrared spectrophotometry. Benzene was among the products evolved in most cases, and acetone was produced during exposure to heat in air. Catalyst fragments or other incorporated impurities affected initiation at very mild conditions. Susceptibility to degradation increased with increasing oxygen content and unsaturation of the untreated polymer. Pyrolysis studies indicated a two stage degradation: (1) dehydrochlorination, and (2) decomposition of the resultant polyene chain. Color formation was attributed to both oxidation and conjugated unsaturation because exposure in air following exposure in a vacuum, and vice versa, caused bleaching of the degraded polymer.

1. Introduction

The degradation of poly(vinyl chloride) has been studied extensively [1 to 16]² because of the commercial importance of this material. The mechanism of decomposition has not been resolved and the initiation step is especially elusive. Druesdow and Gibbs [7] suggested peroxides and catalyst residues as possible sites for initiation of degradation. Fox [4] and his coworkers proposed random splitting out of hydrogen chloride, and Arlman [8, 13] suggested end initiation plus random oxidation. Baum and Wartman [16] reported that the sites for initiation are chain ends at about 150° C and tertiary chlorine atoms above 190° C.

Dehydrochlorination is generally accepted as the propagation step. An allyl-chloride-type reaction is considered as the probable mechanism. However, there are other products from and changes occurring in the polymer. Mack [15] suggested that, in the presence of oxygen, dehydrochlorination and consequent development of conjugated double bonds compete with oxidation of the conjugated system. Both chain scission and crosslinking have been observed [1, 2, 3, 7], often simultaneously.

The identification, measurement of the amount evolved, and rate of evolution of the products on exposure to laboratory weathering or pyrolysis [18 to 22] are among the most frequently used methods for investigating the degradation process. The evolution of hydrogen chloride has been studied in a vacuum, oxygen, air, nitrogen, hydrogen, and hydrogen chloride. Wilson [11] found another product, a condensable gas, which he identified as water. In his work on *sec*-butyl chloride as a prototype of poly(vinyl chloride), Kenyon [1] found carbon dioxide, methane, hydrogen chloride, and masses at 95, 97, 110, and 112 among the gaseous products analyzed by mass spectrometry. Benzene has been identified as a product of pyrolysis [18 to 22].

The complexity of the situation has led to many apparent contradictions. Some investigators have proposed that the loss of hydrogen chloride is autocatalytic [3 to 7], others deny this [13], and still

others have found autocatalysis only in certain atmospheres [1, 3, 7, 15]. Color formation and loss of hydrogen chloride are usually considered as related, but Wilson [11] suggested that the color developed on degradation was at least partially due to the action of light on oxygen-containing impurities. Another source of controversy has been whether color in the degraded polymer is bleached in the presence of oxygen [5 to 10].

This paper describes an attempt to clarify some aspects of the degradation process in poly(vinyl chloride). The effects of several different initiators on the stability of poly(vinyl chloride) on exposure to heat and to ultraviolet radiant energy were investigated. Several exposures were conducted in a vacuum to isolate breakdown of the basic polymer from oxidative degradation. Analyses of the gaseous degradation products and the polymer residue were made at various stages in the treatments to follow the chemical structural changes. Color changes were studied in the hope of correlating them with the structural changes or conditions of exposure.

2. Material and Procedures

2.1. Material

Table 1 lists the four poly(vinyl chloride) polymers used in this investigation. The polymers catalyzed with benzoyl peroxide and 2-azo-bis(isobutyronitrile), respectively, were polymerized from vinyl chloride monomer distilled directly from a storage cylinder into glass tubes containing the catalysts. The tubes containing the monomer, frozen under liquid nitrogen, were sealed under vacuum. Polymerization was accomplished by immersion of the tubes in a water bath at 40° C for 3 days. For the gamma-initiated polymer, the vinyl chloride monomer was fractionally distilled under essentially equilib-

TABLE 1.—Description of poly(vinyl chloride) materials

| | |
|--------------|--|
| γ-PVC..... | Vinyl chloride bulk-polymerized in a vacuum by exposure to gamma (Co-60) radiation. |
| bp-PVC..... | Vinyl chloride bulk-polymerized in a vacuum, with initiation by 0.10-mole percent benzoyl peroxide. |
| azo-PVC..... | Vinyl chloride bulk-polymerized in a vacuum, with initiation by 0.02-mole percent 2-azo-bis(isobutyronitrile). |
| 101-PVC..... | Geon 101, supplied by the B. F. Goodrich Chemical Co. |

¹ This paper was presented before the Division of Polymer Chemistry at the 130th meeting of the American Chemical Society in Atlantic City, New Jersey, Sept. 16-21, 1956.

² Figures in brackets indicate literature references at the end of this paper.

rium conditions. A 33-in. column packed with glass helices was used. The middle third of the distillate was redistilled into glass tubes, which were sealed as above, and the tubes were then inserted in a 0.3-curie cobalt-60 source. The center of each tube was 1.5 in. from the center of the source. The time of exposure was approximately 270 hr.

The three laboratory-prepared polymers were in the form of solid bars when polymerization was completed. These bars were pulverized with a stainless-steel mortar and pestle under liquid nitrogen. The fractions of these polymers and of the commercial polymer that passed through the U. S. Standard No. 325 Sieve (nominal opening 44μ) were used for these experiments.

The polymers were studied in powder form. Poly(vinyl chloride) films were not used because they retain the polar solvents necessary to dissolve the polymers. This can interfere with both the mechanism of degradation and the interpretation of analytical data. Pressed pellets of the polymer are not satisfactory because they provide a very small surface to volume ratio in addition to being partially degraded as a result of the heat required in the pelleting operation.

A typical sample used for an experiment weighed from 0.15 to 0.30 g. The choice of sample size was a compromise between the desire for a monoparticle layer in the exposure tube and the necessity for sufficient pressure from the gaseous degradation products to make mass spectrometric analysis practical.

2.2. Equipment

The polymer powder samples were exposed, in quartz tubes, to various conditions of heat or ultraviolet radiant energy or both, in a vacuum and in air. The exposure tube, exposure chamber, and general procedure have been described previously [24]. The only alteration was the use of F-1 fluorescent sunlamps in place of RS sunlamps for the ultraviolet radiant energy exposures. Six F-1 lamps were mounted in banks of three in planes 3 in. above and below the polymer samples.

2.3. Exposures and Analytical Procedures

The major experimental work consisted of exposure of the same samples of the four polymers to the following three conditions, in sequence: (1) Ultraviolet radiant energy, in a vacuum, at $45^\circ \pm 2^\circ$ C for 100 hr; (2) $100^\circ \pm 2^\circ$ C, in a vacuum, for 100 hr; and (3) $100^\circ \pm 2^\circ$ C, in air, for 100 hr. The gaseous degradation products evolved during each stage were analyzed by mass spectrometry. Color determinations were made after each treatment, using the Munsell colors of the Intersociety Color Council-National Bureau of Standards (ISCC-NBS) Method of Designating Colors. Samples of the polymer powder were removed from duplicate tubes after each exposure for infrared analysis. The powder removed for infrared analysis was pelleted with potassium bromide [23], and a sodium chloride prism was used to determine the infrared spectrum in the 2- to $15\text{-}\mu$ region.

Several additional experiments and analyses were made. 101-PVC was exposed to 100°C , in air, for 25 hr, in an attempt to induce hydroperoxide formation, prior to a sequence of exposures and analyses, as described above. 101-PVC and azo-PVC were exposed to 100°C , in a vacuum, for 200 hr, with mass spectrometric analyses of the gaseous products after 1, 3, 5, 10, 20, 30, 50, 100, and 200 hr; 101-PVC was used in a similar experiment in which ultraviolet radiant energy was used in place of heat. 101-PVC was exposed to 100°C in a vacuum for 150, 288, and 400 hr; to ultraviolet radiant energy at 50°C in air, for 400 hr; and to ultraviolet radiant energy at 45°C , in a vacuum, for 150, 288, and 400 hr.

Samples of 101-PVC and γ -PVC were pyrolyzed in a small evacuated tube furnace. The gaseous products were passed directly into a mass spectrometer. The temperature of pyrolysis was raised in steps from 87° to 429°C , and the mass spectra were recorded at each step. The equipment, method, and some of the results of this pyrolysis have been described by Bradt [19, 20].

3. Results

3.1. Analysis of Original Polymers

Table 2 shows the results of the oxygen-content determinations on the four polymers. The two methods used are similar, and the results can be compared directly.

Infrared absorption spectra of the untreated polymers are shown in figure 1. The γ -PVC polymer (dotted line) shows a very weak absorption at 6.27μ , which is attributed to stretching vibrations of conjugated C=C structures [30, p. 31]. The double-bond structure was probably formed as a result of some dehydrochlorination of the polymer while exposed to gamma radiation. Mass spectrometric analysis of the gases above the γ -PVC polymer immediately after polymerization showed a small amount of hydrogen chloride. 101-PVC (solid line) has a weak band at 6.05μ assigned to C=C stretching of a nonconjugated nature [30, p. 31]. The presence of double bonds in the untreated 101-PVC may also be due to loss of hydrogen chloride during polymerization [15, 17]. Azo-PVC (dashed and dotted line) shows a weak absorption at 9.83μ , which was not identified, and a generally lower transmittance. There also appears to be a very weak absorption at about 6.27μ , as in

TABLE 2. Oxygen content of poly(vinyl chloride) polymers

| Polymer | Oxygen |
|--------------------|------------|
| 101-PVC..... | % a0.90 |
| γ -PVC..... | b. 21 |
| bP-PVC..... | b. 65 |
| azo-PVC..... | b. 43 |

^aBy the method of Walton, McCulloch, and Smith, J. Research NBS **40**, 443 (1948) RP1889. Oxygen content reported here refers to $<44\text{-}\mu$ particles used in this investigation; the oxygen content of the bulk 101-PVC was 0.18 percent as measured by the same method.

^bBy a modification of the Unterzaucher direct microdetermination of oxygen, S. Ishihara, unpublished.

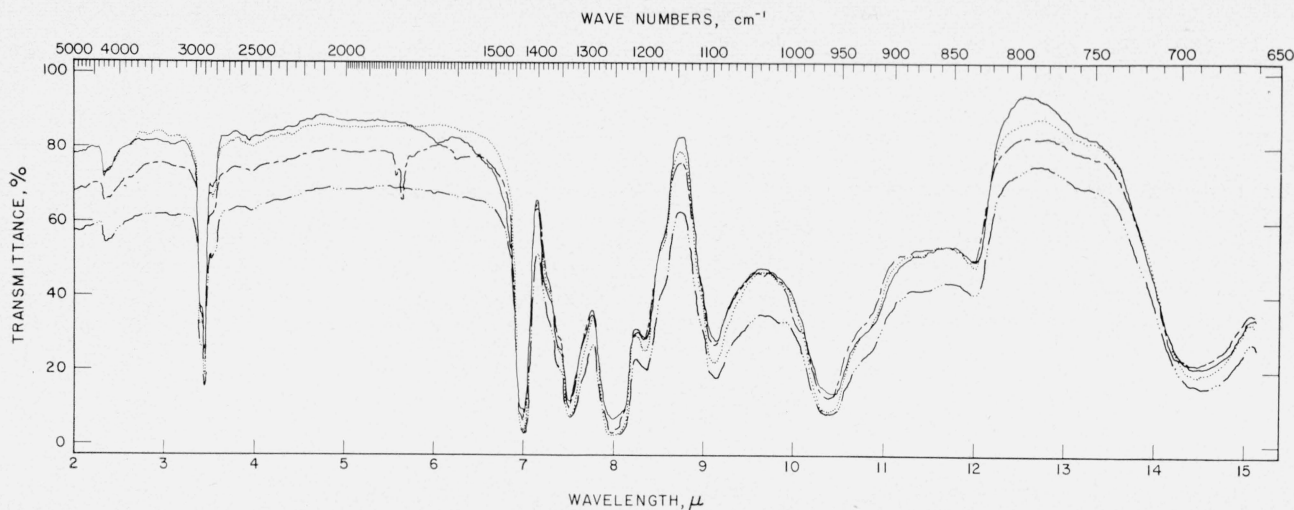


FIGURE 1. Infrared spectra of the poly(vinyl chloride) polymers studied.

101-PVC; --- γ -PVC; bp-PVC; - · - · - azo-PVC.

γ -PVC. In addition to absorptions at 5.57 and 5.64 μ assigned to carbonyl vibrations in the catalyst used [30, p. 111], bp-PVC (dashed line) has a band at 6.22 μ attributed to C=C stretching vibrations. The band at 10.08 μ is probably due to unreacted catalyst [30, p. 106].

An absorption around 12 μ in the region associated with hydroperoxide absorption by Shreve et al. [25] was present in about equal amounts in all the polymers. No changes were observed in this absorption either as a result of degradative treatment of the polymer or during the attempt to induce hydroperoxide formation. Krimm and Liang [31] assign this band to chain stretching in the polymer.

3.2. Mass Spectrometric Analysis of Degraded Polymers

The gaseous degradation products evolved by the polymers on exposure to ultraviolet radiant energy are shown in table 3. The γ -PVC gave 50 to 80 percent less gaseous products than the other polymers, and showed less discoloration as a result of the exposure. The benzene and large amount of carbon dioxide from the bp-PVC polymer were attributed to breakdown of the catalyst used. Hydrogen was a product of 101-PVC only, and

TABLE 3. Gaseous products evolved by poly(vinyl chloride) exposed to ultraviolet radiant energy in a vacuum at 45° C for 100 hr

| Product | Amount evolved per gram of sample— | | |
|--------------------------------------|-------------------------------------|-----------------------------|-------------------------------------|
| | 101-PVC | bp-PVC | γ -PVC |
| | <i>Micromoles</i> | <i>Micromoles</i> | <i>Micromoles</i> |
| Hydrogen chloride..... | 4.3 | 4.6 | 0.9 |
| Water..... | 1.0 | 1.2 | 1.2 |
| Carbon dioxide..... | 1.0 | 13.5 | 1.1 |
| Carbon monoxide and/or nitrogen..... | 1.1 | 0.0 | 0.9 |
| Benzene..... | 0.0 | .6 | .0 |
| Hydrogen..... | .6 | .0 | .0 |
| Final color ^a | 10.0 YR 8/4 (pale orange yellow) | 5.0 YR 5/5 (light brown) | 7.5 YR 9/2 (pale yellowish pink) |

^a According to the Munsell System and the ISCC-NBS Method of Designating Colors.

appeared at each stage of the degradation. The colors developed after the exposure to ultraviolet radiant energy are shown for purposes of comparison. The intensity of the color for any sample correlates with the total amount of products reported for that sample, but not with the amount of hydrogen chloride reported for that sample.

The 101-PVC, exposed at 100° C in air for 25 hr prior to exposure to ultraviolet radiant energy, gave results essentially the same as obtained with 101-PVC without pretreatment. The pretreatment apparently did not induce formation of hydroperoxides in the polymer.

The same samples that were exposed to ultraviolet radiant energy as described above were further exposed to heat in a vacuum. The results obtained with bp-PVC, shown in table 4, are typical of those from the other polymers with two exceptions. The products from γ -PVC were too small to measure in the mass spectrometer, and the benzene evolved by bp-PVC was about three times as much as was evolved by the other polymers.

The mass spectrometer does not measure hydrogen chloride accurately because of adsorption on the walls of the expansion chamber [26]. The presence of water vapor and carbon dioxide in the mass spectrometer background and as products of poly(vinyl chloride) degradation further complicate analysis. Since efforts to evaluate these factors were unsuccessful, the values reported for hydrogen chloride, water, and carbon dioxide must be con-

TABLE 4. Gaseous products evolved by bp-PVC polymer exposed to 100° C in a vacuum for 100 hr

Prior treatment: 100-hr exposure to ultraviolet in a vacuum at 45° C

| Product | Amount evolved per gram of sample— | |
|------------------------|------------------------------------|-------------------|
| | A | B |
| | <i>Micromoles</i> | <i>Micromoles</i> |
| Hydrogen chloride..... | 28.1 | 17.4 |
| Water..... | 1.9 | 9.1 |
| Carbon dioxide..... | 0.9 | 1.1 |
| Benzene..... | .3 | 0.2 |

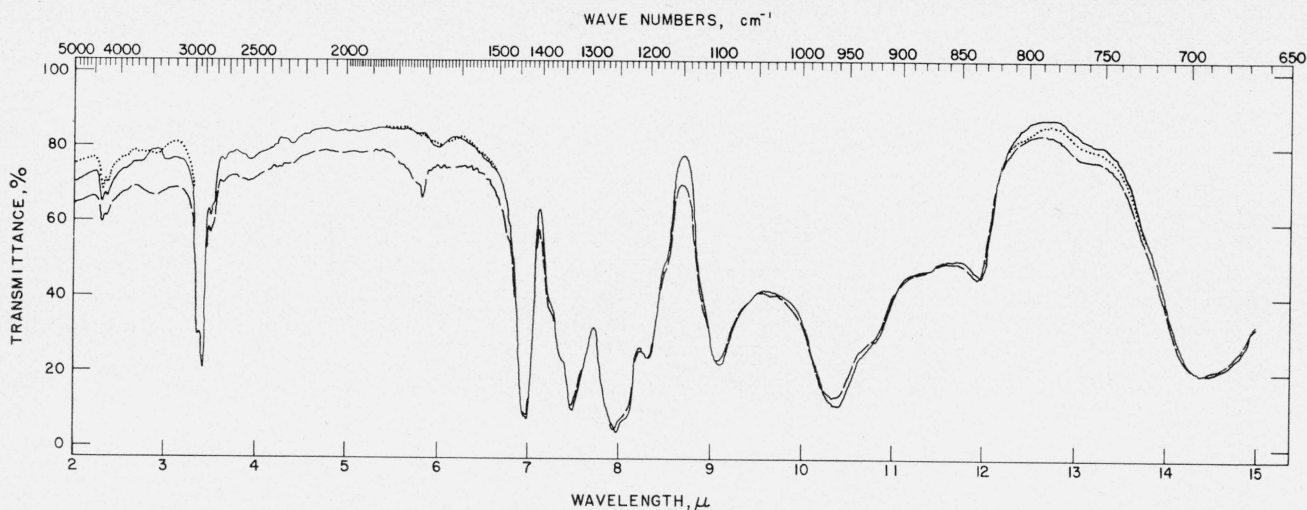


FIGURE 2. Infrared spectra of 101-PVC subjected to degradation.

— Untreated; - - - - - 100-hr exposure to ultraviolet in a vacuum at 45° C.; — — — — — 100-hr exposure to ultraviolet in a vacuum at 45° C, plus 100-hr exposure at 100° C, in a vacuum, plus 100-hr exposure at 100° C in air.

sidered as approximations. Comparison of the results of experiments A and B in table 4 gives an indication of the poor reproducibility obtained when measuring hydrogen chloride and water simultaneously in the mass spectrometer. The example given is an extreme case for duplicate measurements.

The polymer samples previously exposed to ultraviolet radiant energy and to heat in a vacuum were finally exposed to heat in air. The water and carbon dioxide frozen from the air by liquid nitrogen when the air was being pumped from the tubes prior to mass spectrometric analysis masked these gases as possible degradation products. No hydrogen chloride was detected. About 0.1 micromole of benzene per gram of sample was found in the products of γ -PVC and bp-PVC, but not in the products of 101-PVC. Hydrogen was again a product of 101-PVC. From 2 to 23 micromoles of acetone per gram of sample were found in the products of all the polymers except γ -PVC, where the results were inconclusive because one sample showed no acetone and the other was accidentally contaminated with acetone.

TABLE 5. Gaseous products evolved by 101-PVC polymer in 3-hr exposures to ultraviolet radiant energy and to 100° C in a vacuum

| Product | Amount evolved per gram of sample in 3 hr of exposure to— | |
|--------------------------------------|---|------------|
| | Ultraviolet | Heat |
| | Micromoles | Micromoles |
| Hydrogen..... | 0.36 | 0.20 |
| Water..... | 2.38 | 1.20 |
| Carbon monoxide and/or nitrogen..... | 0.53 | 0.27 |
| Oxygen..... | .00 | .02 |
| Carbon dioxide..... | .36 | .51 |
| C ₇ H ₁₆ | .00 | .11 |
| C ₇ H ₁₄ | .00 | .41 |
| Benzene..... | Trace | .02 |
| Toluene..... | Trace | .10 |
| Styrene..... | 0.00 | .04 |
| Alkyl benzene..... | .00 | .02 |

The products evolved by 101-PVC after 3 hr of exposure to ultraviolet radiant energy are shown in table 5. Traces of hydrogen chloride were reported after 50 and 100 hr of exposure, and hydrogen chloride was the major product after 200 hr of exposure. The results after 3 hr of exposure to heat are also listed in table 5. The amount of hydrogen chloride evolved after 200 hr at 100° C was about 13 times as much as was reported for a 200-hr exposure to ultraviolet radiant energy.

Azo-PVC was also exposed to 100° C in a vacuum for 200 hr. Except for considerable amounts of unidentified nitriles [27] found in the first 30 hr, the amounts and types of products were similar to those found with the other polymers.

Uninterrupted exposures of 101-PVC to 100° C in a vacuum and to ultraviolet radiant energy at 45° C in a vacuum for 150, 288, and 400 hr resulted in hydrogen chloride, water, hydrogen, carbon monoxide, and carbon dioxide, plus small amounts of unidentified hydrocarbons. Benzene and toluene were found after exposure to heat but not after exposure to ultraviolet radiant energy.

3.3. Infrared Analysis of Degraded Polymers

The infrared absorption spectra obtained after carrying out the progressive exposure series on 101-PVC are shown in figure 2. Exposure to heat in a vacuum after exposure to ultraviolet produced no substantial change in the spectrum. The changes around 3 μ reflect compensation difficulties in the OH region due to water absorption in some potassium bromide pellets. Exposure to heat in air removed the weak band at 6.05 μ attributed to double bonds, and produced a broad carbonyl absorption band around 5.85 μ . The changes observed are of about the same order as, or larger than, those occurring in the other polymers under the same conditions.

Figure 3 shows the 5- to 7- μ region of the spectra of bp-PVC. The original polymer shows absorptions at 5.57 and 5.64 μ attributed to residual benzoyl

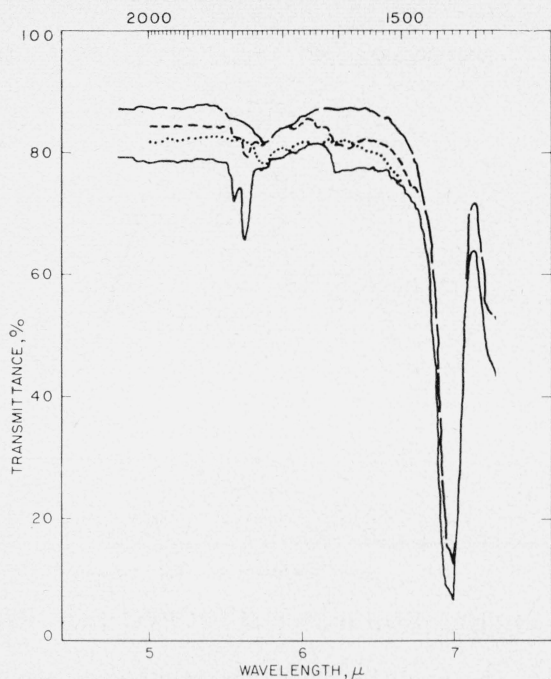


FIGURE 3. Infrared spectra of bp-PVC subjected to degradation.

— Untreated; - - - - - 100-hr exposure to ultraviolet in a vacuum at 45° C; ······ 100-hr exposure to ultraviolet in a vacuum at 45° C, plus 100-hr exposure at 100° C in a vacuum; — · — · — 100-hr exposure to ultraviolet in a vacuum at 45° C, plus 100-hr exposure at 100° C in a vacuum, plus 100-hr exposure at 100° C in air.

peroxide catalyst, and at 6.22 μ attributed to conjugated double bonds. After exposure to ultraviolet radiant energy, the absorptions at 5.77 and 5.64 μ decreased considerably, whereas the absorption at 6.22 μ increased slightly. After subsequent exposure to heat in a vacuum, the absorptions at 5.57, 5.64, and 6.22 μ disappeared, and a carbonyl band appeared at 5.85 μ . Exposure to heat in air caused a rise in transmittance and a stronger and broader carbonyl absorption.

Figure 4 contains the spectra of untreated 101-

PVC (solid line) and 101-PVC exposed to ultraviolet radiant energy in air at 50° C for 400 hr (dashed line). A wide absorption band extending from 2.7 to 4 μ with shoulders at about 2.85, 3.03, 3.50, and 3.77 μ is present in the spectrum of the degraded material. The absorption occurring between 3.7 and 4 μ is indicative of the OH stretching vibration of strongly hydrogen-bonded OH groups [30, p. 142]. The absorption around 2.7 to 2.85 μ has been assigned to the OH valence stretching of the unbonded hydroxyl group [30, p. 85], and the absorption in the 2.85- to 3.15- μ range may be caused by the OH vibration of intermolecular and intramolecular hydrogen bonds. The broad, intense carbonyl absorption in the 5.8- to 5.9- μ region is probably caused by the C=O stretch in a variety of structures such as aldehydes, ketones, acids, etc. The shoulder at 6.05 μ may indicate the presence of unconjugated double bonds.

Figure 5 shows the spectra of 101-PVC after exposure to 100° C in a vacuum for 150 and 400 hr. After 150 hr (dotted line), the absorption at 6.05 μ , attributed to unconjugated unsaturation, changed very little. Slight absorptions in the 6.25- and 6.65- μ regions indicate some formation of conjugated double bonds or possibly some aromatics. The absorption at 5.8 μ is attributed to carbonyl formation. The oxygen must have come from the polymer because mass spectrometry gave no evidence of leakage in the exposure tube. Except for an increase in the carbonyl absorption, there was little change after 400 hr of exposure.

3.4. Color Changes

Table 6 shows the color developed by each polymer at each stage in the set of experiments described in section 3.2. The higher the number before the slash mark, the lighter the color; the higher the number after the slash mark, the more intense the hue.

A comparison of the data in the second and third columns shows that oxygen causes bleaching of the color developed in polymers degraded in a vacuum. The γ -PVC developed the least discoloration. Bp-

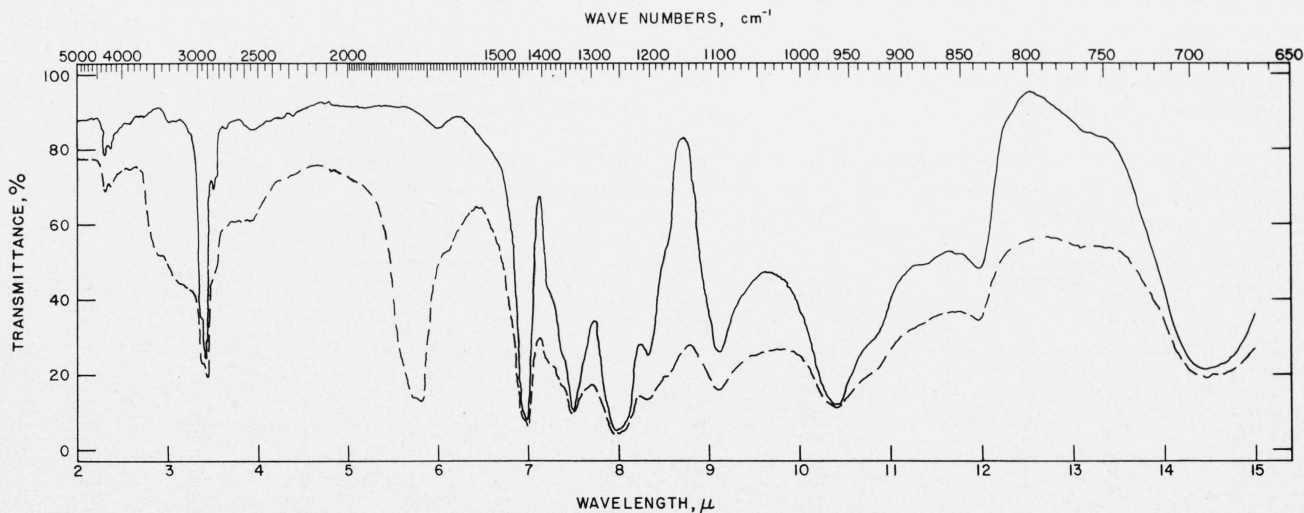


FIGURE 4. Infrared spectra of 101-PVC before and after exposure to 400 hr of ultraviolet in air at 50° C.

— Untreated; - - - - - treated.

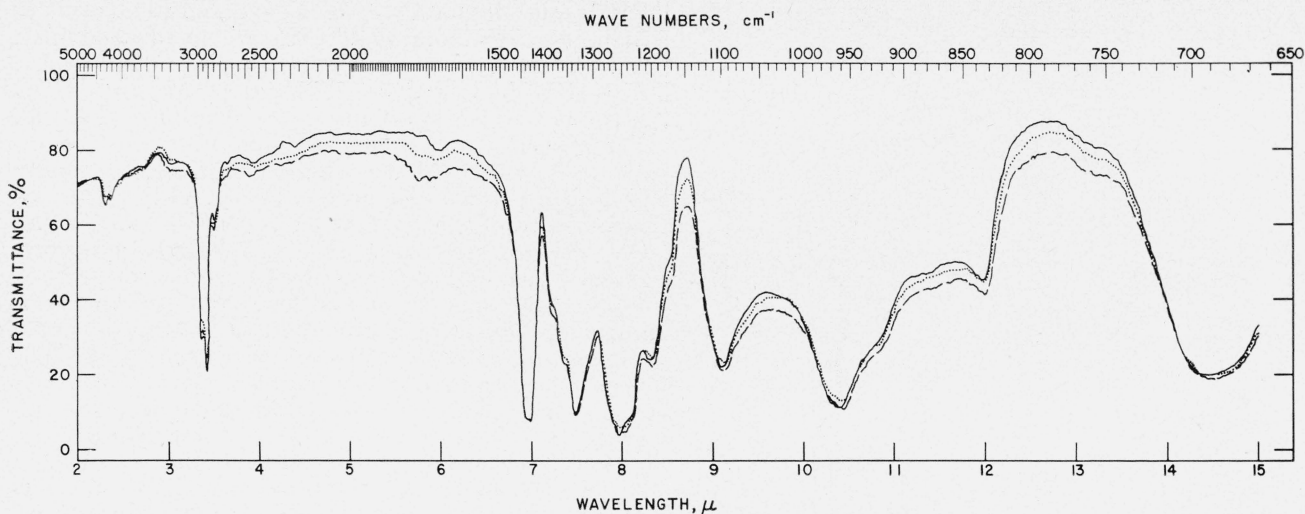


FIGURE 5. Infrared spectra of 101-PVC subjected to heat degradation.

————— Untreated; - - - - - 150-hr exposure at 100° C in a vacuum; - · - · - 400-hr exposure at 100° C in a vacuum.

TABLE 6. Colors developed in degraded poly(vinyl chloride)

| Polymer | Munsell designation and color ^a after exposure to— | | |
|---------------|---|---|--|
| | 100 hr of ultraviolet in a vacuum | Plus 100 hr at 100° C in a vacuum | Plus 100 hr at 100° C in air |
| 101-PVC | 10.0 YR 8/4 (pale orange yellow) | 2.5 R 3.5/4 (grayish red-dark red) | 7.5 YR 7/4 (light yellowish brown) |
| γ -PVC | 7.5 YR 9/2 (pale yellowish pink) | 10.0 R 7.5/4 (moderate yellowish pink) | 7.5 YR 9/2 (pale yellowish pink) |
| bp-PVC | 5.0 YR 5/5 (light brown) | 7.5 P 7/4 (pale purple) | 10.0 R 8/2 (pale yellowish pink-grayish yellowish pink) |
| azo-PVC | 7.5 YR 8/3.5 (pale orange yellow) | 7.5 YR 7/4 (light yellowish brown) | 10.0 YR 8/4 (pale orange yellow) |

^a The ISCC (Intersociety Color Council)—NBS Method of Designation Color.

PVC discolored most on exposure to ultraviolet radiant energy and 101-PVC discolored most on subsequent exposure to heat. Bp-PVC bleached slightly and changed color on exposure to heat after exposure to ultraviolet radiant energy.

3.5. Pyrolytic Degradation of 101-PVC and γ -PVC

The relative ratios of the major products evolved during continuous pyrolysis of γ -PVC and 101-PVC at various temperatures as analyzed by mass spectrometry are given in table 7. A small amount of hydrogen chloride was evolved from 101-PVC at 127° C. Benzene was a product of both polymers at about 175° C, along with relatively large amounts of hydrogen chloride. The maximum evolution of hydrogen chloride from 101-PVC occurred at 220° C, whereas for γ -PVC the maximum was at 238° C. The largest evolution of benzene and measurable amounts of mass 91, naphthalene, and anthracene were observed in the 220° to 240° C range. Above 300° C very little hydrogen chloride was evolved, and mass 91 became the major product. Mass 91 represents the principal decomposition product of alkyl-aromatic compounds. It was accompanied by a large number of different hydrocarbons of varying degrees of saturation. At 389° C there were products of every mass number from 78 to 600, the limit of the resolving power of the mass spectrometer. Beyond mass 200 the amounts of each product were

TABLE 7. Gaseous products evolved by 101-PVC and γ -PVC during pyrolysis

| γ -PVC | | | | 101-PVC | | | | | | Largest mass number | Probable composition |
|---------------|--|-----|-------|---------|--|-------|-------|-------|-------|---------------------|---------------------------------|
| Temp | Peak heights, in scale divisions for mass numbers— | | | Temp | Peak heights, in scale divisions for mass numbers— | | | | | | |
| | 36 | 78 | 91 | | 36 | 78 | 91 | 128 | 178 | | |
| °C | | | | °C | | | | | | | |
| 172 | 24 | 0.5 | ----- | 127 | 7 | ----- | ----- | ----- | ----- | ----- | ----- |
| 190 | 164 | 27 | ----- | 179 | 218 | 12.5 | ----- | ----- | ----- | ----- | ----- |
| 214 | 736 | 52 | ----- | 194 | 440 | 48 | ----- | ----- | ----- | 128 | C ₁₀ H ₈ |
| 238 | 2,416 | 94 | ----- | 220 | 2,294 | 244 | 4 | 14 | 3.5 | 179 | C ₁₄ H ₁₁ |
| 251 | 338 | 6 | 1 | 250 | 1,015 | 45 | ----- | ----- | ----- | ----- | ----- |
| 284 | 18 | 9 | 14 | 280 | 1,290 | 43 | 13 | 13.5 | 2.5 | 179 | C ₁₄ H ₁₁ |
| | | | | 306 | 126 | 51 | 72 | 40 | 10.5 | 192 | C ₁₅ H ₁₂ |
| 331 | 4 | 4 | 26 | 335 | 59 | 37 | 123 | 67 | 26 | 253 | C ₂₀ H ₁₃ |
| 381 | 1.8 | 3.9 | 26 | 389 | 3.5 | 11.5 | 89 | 21 | 31 | 596 | ----- |

about equal, and between mass 400 and mass 600 the spectrum resembled a sine wave with maxima at all the even mass numbers.

The γ -PVC sample was smaller than the 101-PVC sample, and this is reflected in the lower values for γ -PVC at each step.

4. Discussion and Conclusions

The stability of poly(vinyl chloride) is a function of: (1) the structure of the polymer, including structural deviations and chemically or physically incorporated impurities; (2) the processing and storage history of the polymer; and (3) the conditions of exposure, including the ambient atmosphere and the wavelength and intensity of the incident energy. Recognition of these factors, combined with the results obtained in this investigation, lead to possible explanations that may account for some of the observations recorded here and in the literature.

4.1. Initiation

Initiation of degradation probably occurs at several different sites, the particular polymer and the conditions of exposure being determining factors. The susceptibility to degradation of the polymers studied increased both with the oxygen contents of the polymers and with the initial unsaturation. The effects of the two were not separated, but both are probably factors of some importance in initiation.

Several investigators [7, 8, 13] have proposed that oxygen contained in a polymer is a factor in degradation, but the actual mechanism by which that oxidation, presumably occurring during polymerization, contributes to the decomposition of the polymer has not been isolated. Although the oxygen contents of the polymers studied here may in part be due to peroxidic structures, none were found; neither were any other oxygenated structures except in the case of bp-PVC where an excess of an oxygen-containing catalyst was apparent both in the infrared spectra and in the gaseous degradation products.

The presence of unsaturation in undegraded poly(vinyl chloride) has been established by others [8, 9, 16]. Baum and Wartman [16] have shown that it occurs at chain ends, probably as a result of disproportionation, and is a major factor in initiation of degradation at 150° C.

The presence of catalyst fragments has also been proposed as providing sites for initiation of degradation [7]. The importance of impurities incorporated chemically or physically was illustrated here by the gaseous products that resulted from the decomposition of catalysts, soap, etc. when 101-PVC and azo-PVC were exposed to heat in a vacuum for short periods of time and when bp-PVC was exposed to ultraviolet radiant energy in a vacuum, even over extended periods of time. In the latter case the decomposition of the catalyst could be followed in the infrared absorption spectra as well as by analysis of the gaseous degradation products. Since the exposure conditions were little more stringent than actual service conditions, and since γ -PVC, which did not contain any catalyst residue,

was much more stable than the other polymers, it is possible that incorporated impurities are a major factor in instability under normal service conditions.

Initiation of degradation of γ -PVC was probably due to oxygenated or unsaturated structures in the polymer. If this is so, it might be said that the earlier and greater instability of the other polymers was solely due to the greater amount of oxygenation and unsaturation in these polymers. Both were probably of considerable importance, but the very early occurrence of the decomposition products from incorporated impurities and the fact that the incorporated impurity was largely responsible for the high oxygen content in bp-PVC seem to indicate that impurities play a large role in mild conditions of exposure. The failure of other investigators to find any effect from incorporated impurities may be attributed to the transitory nature of the reaction and to the possibility that at the more stringent conditions usual in degradation studies, other factors such as unsaturation assume greater importance. Thus, at relatively low temperatures some labile groups may become active, and as the temperature is raised other labile groups, possibly more predominant but relatively dormant at the lower temperature, may become so active as to obscure the effects of the less prevalent structures. A somewhat parallel situation occurred when Baum and Wartman found unsaturation of primary importance at 150° C and tertiary chlorine assuming a larger role when degradation was carried out at 190° C or higher.

The type and conditions of exposure, especially the wavelength and intensity of the incident energy, have specific degradative effects dependent on the chemical structure of the polymer. For example, bp-PVC is more susceptible to ultraviolet radiant energy, and the 101-PVC and azo-PVC polymers are more susceptible to heat.

4.2. Propagation

After initiation the degradation of poly(vinyl chloride) proceeds in a complex manner. The most obvious feature is dehydrochlorination, which Arlman [13] has shown to be a free-radical reaction. Pyrolysis indicates that two stages actually occur in the degradation of poly(vinyl chloride), exclusive of oxidation reactions. Dehydrochlorination leaves a polyene backbone that further decomposes into a mixture of aliphatic, aromatic, and alkyl-aromatic materials. The first such product observed was benzene, possibly formed by cyclization of unsaturated chain ends [21]. The early appearance of benzene as a product of degradation under mild conditions seems to confirm the mechanism of cyclization and also is another indication of end initiation and a zipper-type reaction. The failure to produce more than a small amount of benzene is attributed to decreased mobility of the chains as unsaturation proceeds and crosslinking occurs. Ultimately, under pyrolytic conditions, sufficient energy is available for random C—C rupture. This accounts for the multitude of other carbon compounds produced in pyrolysis.

In degradation under service conditions oxygen may affect both stages of the degradation of poly(vinyl chloride). Oxidation of both saturated and unsaturated portions of the polymer chain may lead to chain scission and to an increased concentration of free radicals, which may accelerate dehydrochlorination. This has been observed frequently [1, 3, 5, 7]. The presence of ultraviolet radiant energy accelerates oxidation reactions.

The production of acetone is probably due to a mechanism similar to that found by George and Walsh [28, 29]. This would result in chain scission. Whether the necessary oxygen to form the acetone came from the ambient atmosphere or from the oxygen contained in the polymers was not determined. The polymers with higher oxygen contents produced more acetone but acetone only appeared after exposure in air.

The mechanism by which dehydrochlorination occurs has generally been accepted to be of an allylic nature [2, 4, 5, 7, 9], that is, a chlorine atom in the beta position to a double bond requires less energy for removal. However, many of the proposed mechanisms were not presented as free-radical chain reactions, though the occurrence of a free-radical reaction has been established [12, 13]. The mechanism proposed by Stromberg et al [21] combines allylic excitation with a free-radical reaction and can be made to fit any or all of the proposed mechanisms of initiation. It also allows for the effects of oxidation in that oxygenated radicals as well as a chlorine radical freed by allylic excitation may initiate a chain reaction. One minor modification suggested is that removal of a hydrogen atom to start a chain reaction need not necessarily occur adjacent to a double bond.

Crosslinking is possible whenever two chains with free radicals are in proximity. A moderately frequent occurrence of this nature is conceivable. Scission probably occurs principally as a result of oxidative degradation except in pyrolysis, where there is usually sufficient energy available to rupture C—C bonds.

4.3. Color

The degradation of poly(vinyl chloride) is accompanied by a discoloration that has been attributed to the polyene system. It was observed by some investigators that exposure of degraded poly(vinyl chloride) to oxygen led to bleaching of the color, whereas others failed to find this occurring. In view of the results obtained in this study, it seems that two sources of chromophores are possible, from conjugated unsaturation and from oxygenated structures. If a polymer is degraded in a vacuum and exposed to air, the color due to unsaturation may be bleached. A carbonyl absorption in the polymer occurs simultaneously. In the case of degradation on exposure to ultraviolet radiant energy with oxygen present, color formation seems to be due either to oxygenation only or to both types of chromophores. Absorptions due to carbonyls and conjugated unsaturation may be found. Further exposure to oxygen does not lead to bleaching. On the other hand, if a polymer containing both chromo-

phores is subjected to heat in a vacuum, bleaching will also occur as well as a change in hue. A shift in the carbonyl absorption occurs at this stage. Probably the oxygenated chromophore is removed slowly, and if the exposure were carried far enough the color would again increase in intensity. Ultraviolet radiant energy is probably necessary to produce oxygenated chromophores.

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