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The Thermal Stability of Poly(vinyl Chloride) Prepared by Radiation Polymerization

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ABSTRACT

The thermal stability of poly(vinyl chloride) prepared by radiation polymerization has been examined by thermogravimetric analysis, hydrogen chloride evolution, and visible spectra measurements in films and solutions. Radiation polymerized PVC, prepared with relatively high radiation doses, is much less stable than a commercial suspension polymerization PVC. On the other hand, the stabilities of radiation polymerized samples, which had received less than 0.45 Mrad, are comparable with commercial PVC. It is suggested that the allylic

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chlorine atoms produced in the radiolysis of the polymer, concurrent with its formation, are chiefly responsible for the instability of the high doses samples.

INTRODUCTION

Poly(vinyl chloride) (PVC) prepared by radiation-induced polymerization is free from initiator fragments which can sometimes initiate [1-3] dehydrochlorination. This may lead to an increased thermal stability of radiation-polymerized PVC [2, 4]. On the other hand, it has been demonstrated recently that the irradiation of commercial PVC enhances thermal-induced dehydrochlorination [5, 6]. It has been suggested [5] that the enhancement is due to the formation of additional labile structures such as allylic chloride and allyl radicals on irradiation, though the formation mechanism suggested is different from Winkler's well-known free radical chain mechanism [13]. Radiation polymerized PVC may also have more labile structures than the PVC prepared by other methods since both the terminated and the growing PVC chains are exposed to radiation during the radiation polymerization of vinyl chloride. In this work, studies of the thermal stability of radiation-polymerized PVC are reported.

EXPERIMENTAL

Vinyl chloride, more than 99% pure, supplied by the Ethyl Corp., was used as received. A commercial unstabilized PVC (Ethyl Corp.) was used for comparison with radiation polymerized PVC.

Radiation-polymerized PVC was prepared by bulk polymerization as follows. Glass ampules (6-1/2 × 3/4 in.) were filled with 5 ml of vinyl chloride by distillation on a high vacuum line, sealed off under vacuum, and then stored at -78°C. Polymerizations were carried out by subjecting the ampules to gamma rays from a ⁶⁰Co source (U. S. Nuclear Corp. GR-9 irradiator). The dose rate was 0.88 Mrad/hr. The polymerization temperatures were -78°, 0, 25, and 60°C. After irradiation, the ampules were immersed in liquid nitrogen and then opened. The filtered polymer were dried overnight in a vacuum oven and then weighed. A measure of the molecular weight of the polymers was obtained from the intrinsic viscosity determined in cyclohexanone at 25°C. A special sample for NMR measurement was prepared from a 53 vol% solution of vinyl chloride in t-amyl alcohol.

The thermal stability of the PVC samples was determined by three methods: thermogravimetric analysis (TGA), hydrogen chloride evolution measurements, and visible spectra measurements. TGA was carried out using a Perkin-Elmer TGS-1 thermobalance and in the form

of films cast from purified tetrahydrofuran solutions. A polymer sample of 2 to 5 mg was placed in an aluminum pan and the thermobalance chamber was flushed thoroughly with nitrogen before the start of each run. During the run, helium was passed through the chamber at a flow rate of 20 ml/min. TGA was either isothermal (202, 188, 172°C) or dynamic, at a heating rate of 20°C/min. The temperature of the sample pan was calibrated with magnetic standards for both programmed temperature and isothermal studies by the method described by Salovey and Bair [5].

Visible spectra measurements were carried out, at 198°C, both in films and in solutions of the polymers after thermal degradation. In the discoloration studies the films of polymers were prepared by casting from tetrahydrofuran solution on glass plates, followed by drying in a vacuum oven at 40 to 50°C. The films were clamped in an aluminum holder which could be fitted to the spectrometer, and both the film and holder were heated under nitrogen. After plunging into ice water for rapid cooling, they were transferred to a Perkin-Elmer 350 Spectrometer and the visible spectrum was measured.

The rates of dehydrochlorination were measured on solid samples using the degradation apparatus described by Bengough and Sharpe [10]. In this the sample is heated in a test-tube reactor by a vapor bath and the evolved hydrogen chloride titrated with caustic soda. The titration was carried out both manually and automatically. For the latter a Metrohm Combi-Titrator was used. This consists of a pH meter and an automatic titrator connected to a recording burette and gives a continuous record of the amount of alkali required to maintain a solution at a set pH. In all cases the dehydrochlorination measurements were made while the samples were heated in a continuous flow of nitrogen.

The solution discoloration studies were carried out using ethyl benzoate solutions of 10 g/liter. Nitrogen was bubbled through the solutions during thermal degradation. The spectra were measured using 1 cm glass cells with a similar cell containing undegraded polymer solution as a reference.

RESULTS

Table 1 gives the polymerization conditions and the intrinsic viscosities of the poly(vinyl chloride) samples used in the thermal stability studies.

Figure 1 shows a typical dynamic TGA for the commercial PVC heated over the temperature range 0 to 500°C. It is seen that very little weight loss occurs up to about 240°C. The polymer, however, became highly colored during this period. The very rapid weight loss in the vicinity of 300°C is followed by reaching about 60% of the initial

TABLE 1. Polymerization Conditions and Intrinsic Viscosities of PVC Samples Used in the Stability Tests

Sample	Dose rate (Mrad/hr)	Polymerization temp (°C)	Irradiation time (hr)	Total dose (Mrad)	Conversion (%)	$[\eta]$ (dl/g)
Commercial	-	-	-	-	-	0.93
B1	0.88	0	2.5	2.2	89	1.37
B2	0.88	0	0.5	0.44	13	1.32
B3	0.88	0	0.25	0.22	5	1.27
B4	0.14	25	2.0	0.28	43	
B5	0.88	60	0.3	0.26	23	0.67
B6	0.88	-78	15	13.2	20	- ^a
B7 ^b	0.12	0	48	5.75	85	-

^a Insoluble in cyclohexanone.

^b Precipitation polymerization in *t*-amyl alcohol solution (53 vol%). The others were polymerized in the bulk monomer.

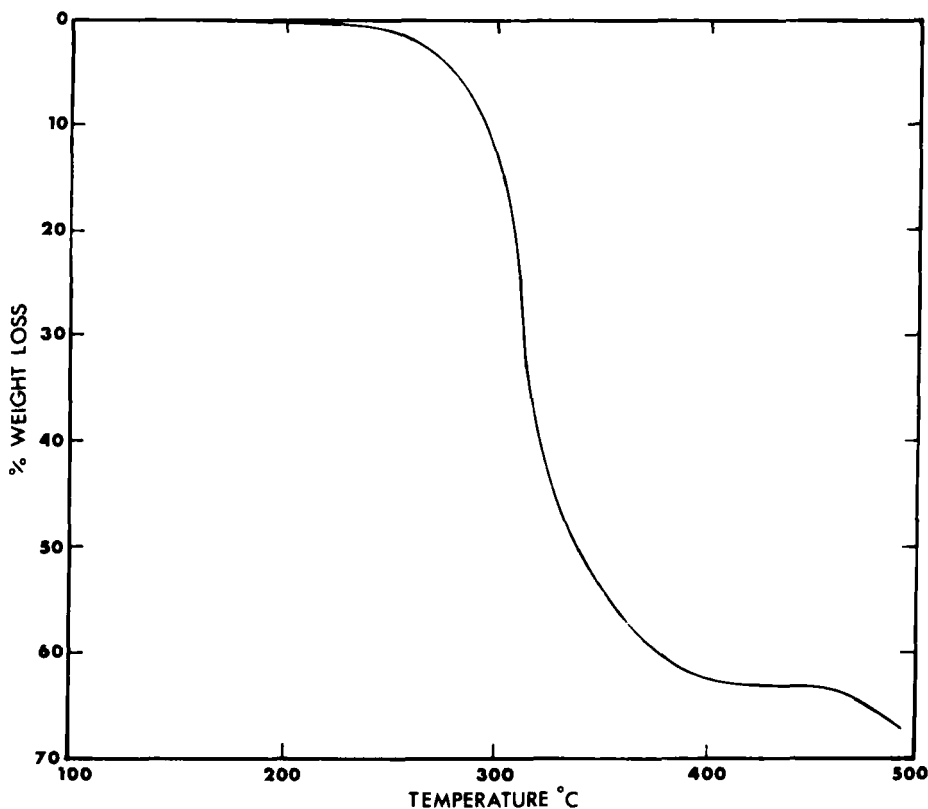


FIG. 1. Thermogravimetric analysis of commercial poly(vinyl chloride) at 20°C/min in helium.

weight, corresponding to the hydrogen chloride content in PVC. Thus the lower temperature weight loss is entirely due to dehydrochlorination [5]. Figure 2 shows dynamic TGA for various samples of PVC between 200 and 300°C, using 40 times the recorder sensitivity as that used to obtain Fig. 1. From Fig. 2 it can be seen that there is a slow but measurable degradation below 240°C in the commercial PVC and a rapid weight loss above this temperature. These results coincide very well with corresponding results in the literature [5, 7]. This rapid weight loss above 240°C is typical of both the commercial and the radiation polymerized samples. In the commercial sample, however, the weight loss curve is much steeper than in the radiation polymerized samples and they occur at a higher temperature. This indicates that the activation energy for

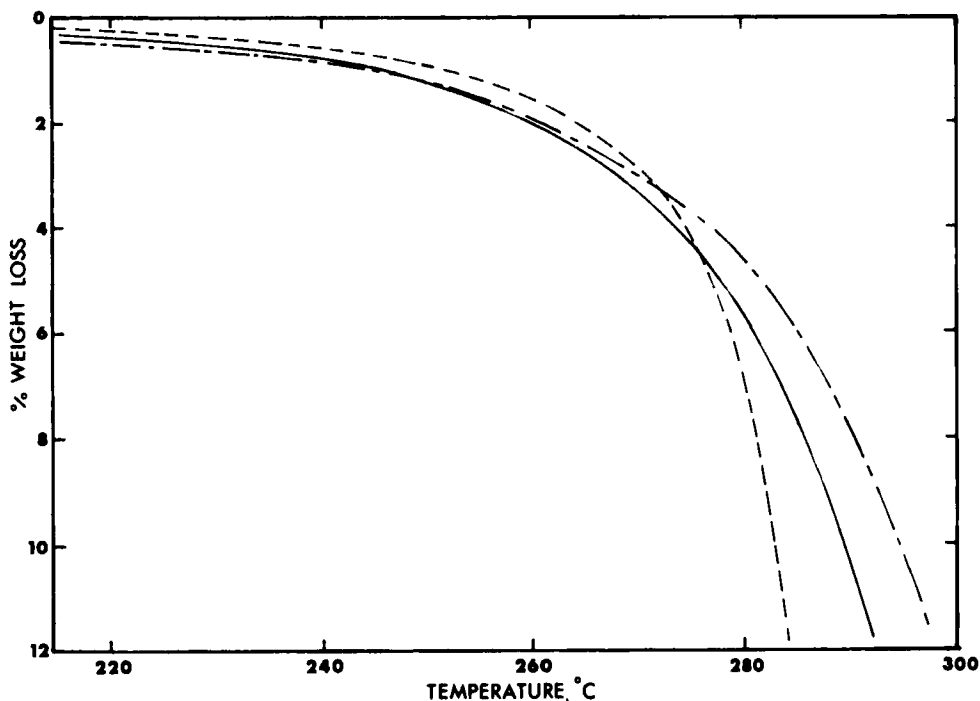


FIG. 2. Thermogravimetric analysis of radiation polymerized and commercial poly(vinyl chloride) at 20°C/min in helium: (—) commercial; (—) Sample B5; (—) Sample B2.

degradation of the commercial PVC is higher than that of the radiation polymerized samples.

The best measure of the relative stability of the PVC samples would be obtained from isothermal studies at temperatures where the initial coloration occurs. Figure 3 shows the isothermal weight loss curves at three temperatures for the commercial polymer and the B1 radiation polymerized PVC. Table 2 gives the rates of weight loss at three temperatures for the polymers. The rates of dehydrochlorination are calculated assuming that all the weight loss is due to the loss of hydrogen chloride, and they are expressed as moles of hydrogen chloride per gram of polymer per second. The results of Table 2 show that, with the exception of B2 at 202°C, the commercial sample degrades more slowly at any given temperature than the radiation polymerized sample. Sample B1 seems to be particularly unstable although the

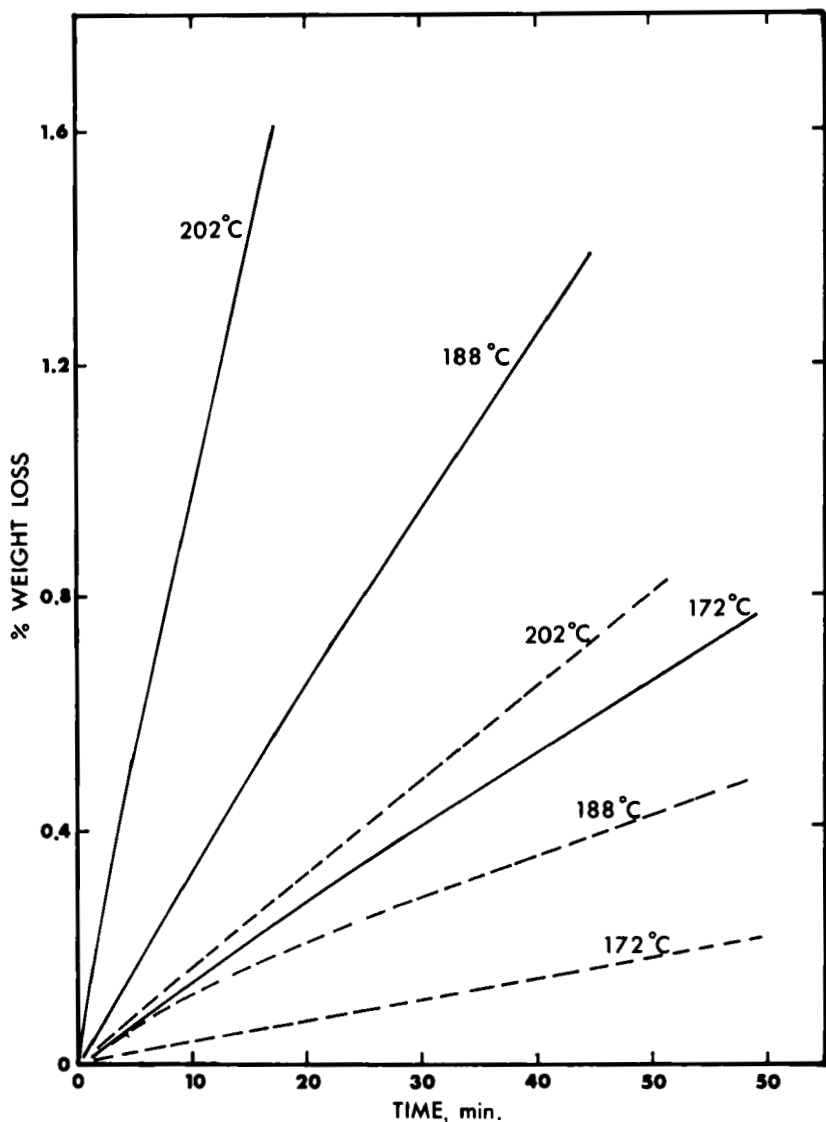


FIG. 3. Isothermal thermogravimetric analysis for radiation polymerized and commercial poly(vinyl chloride) at various temperatures in helium: (—) Sample B1; (---) commercial.

TABLE 2. Thermal Degradation of PVC between 170 and 210°C

Sample	Temperature (°C)	Rate of weight loss (%/min × 10 ²)	Calculated as rate of dehydrochlorination [moles/(g)(sec) × 10 ⁸]
Commercial	202	1.68	7.67
	188	0.38	1.74
	172	0.19	0.87
B1	202	8.8	40.2
	188	3.0	13.7
	172	1.28	5.84
B2	202	1.26	5.75
	188	0.54	2.47
	172	0.32	1.46
B4	202	1.77	8.08
	188	0.60	2.74
	172	0.40	1.83
B5	202	2.08	9.50
	188	0.52	2.37
	172	0.22	1.00

others, within experimental error, approach the stability of the commercial sample at 202°C. Sample B1 is the polymer which has been exposed to one of the highest radiation doses and polymerized to the highest conversion during its preparation.

Table 3 gives the directly measured rates of dehydrochlorination on the powdered polymer together with those calculated from the weight loss (TGA) measurements and the rates of increase in absorbency. Considering the differences in the sample form and methods used, the agreement is reasonably good.

Figure 4 shows the visible spectrum of B5 PVC film after various times of heating under nitrogen. It is the typical multipeak spectrum [8] of degraded PVC, the wavelength of peaks indicating the length of polyene structures formed by hydrogen chloride elimination. Figure 5 is a plot of the total absorbance in the visible region against time of heating for the films of various PVC samples. The absorbance values were obtained by measuring the area between the spectral traces and the trace at zero time. Sample B1 again shows a great difference in stability, whereas the initial increase of absorbance displayed by the other radiation samples are comparable to the commercial PVC. These results are also consistent with the results given in Tables 2 and 3.

TABLE 3. The Effect of Total Radiation Dose on the Thermal Stability of Polymers by Three Different Methods^a

Sample number	Total radiation dose (Mrad)	Temp of polymerization (°C)	dHCl/dt ^b (mole g ⁻¹ sec ⁻¹ × 10 ⁷ , 198°C)	Calculated dHCl/dt from TGA results (moles g ⁻¹ sec ⁻¹ × 10 ⁷)		Rate of increase in absorbance 1,2, etc. in order of decreasing rates at 198°C	
				202°C	188°C	173°C	Film
B6	13.2	-78	3.98	-	-	-	2
B1	2.2	0	5.15	4.02	1.37	0.58	1
B2	0.44	0	3.11	0.58	0.25	0.15	2
B4	0.28	25	1.51	0.81	0.27	0.18	-
B5	0.26	60	1.53	0.95	0.24	0.10	3
B3	0.22	0	-	-	-	-	5
Commercial	0.0	?	1.11	0.77	0.17	0.09	4

^aAll results except TGA at 202°C and last column agree with the stability sequence B1 < B6 < B2 < B4 & B5 < Commercial polymer.

^bMeasured directly, Bengough and Sharpe method [10].

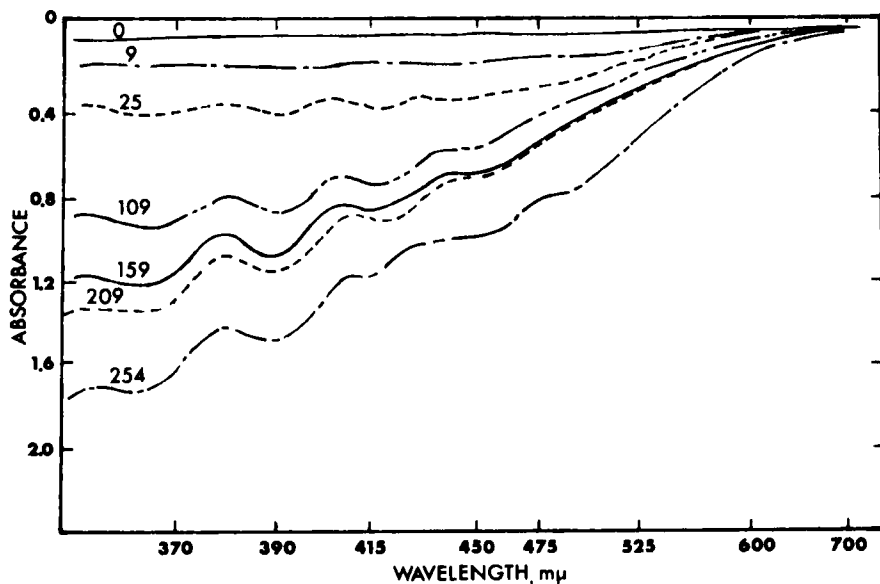


FIG. 4. Absorbance of radiation polymerized poly(vinyl chloride) (Sample B5) film at various times of heating at 198°C: numbers on spectra are minutes at 198°C.

The gaseous diffusion and the catalysis of hydrogen chloride out of the molten polymer can affect the thermal degradation of PVC [9]. It is also difficult to obtain homogeneous mixtures of solid compounds when the effect of solid additives on PVC degradation is investigated. These difficulties are eliminated by studying the degradation in solution. The thermal degradation of PVC in inert solvents such as ethyl benzoate have been extensively investigated by Bengough and co-workers [10]. Figure 6 shows the visible spectrum of PVC solution in ethyl benzoate after various times of heating under nitrogen. It can be seen that the visible spectrum is similar to Fig. 3 although the color development appears to occur faster, even when the polymer concentration in the solution is only 10 g/liter. Figure 7 is a plot of the total absorbance against time of heating for polymer solutions. Samples B1 and B6, exposed to the highest radiation doses, are much less stable than the commercial PVC. On the other hand, Sample B3, which had received the lowest radiation doses, is more stable than the commercial PVC. The stability of Sample B5 appears to be similar to the commercial PVC. The solution data also coincide reasonably well with the polymer films data in Table 2, the powdered polymer data in Table 3, and with the total visible absorbance of films in Fig. 5.

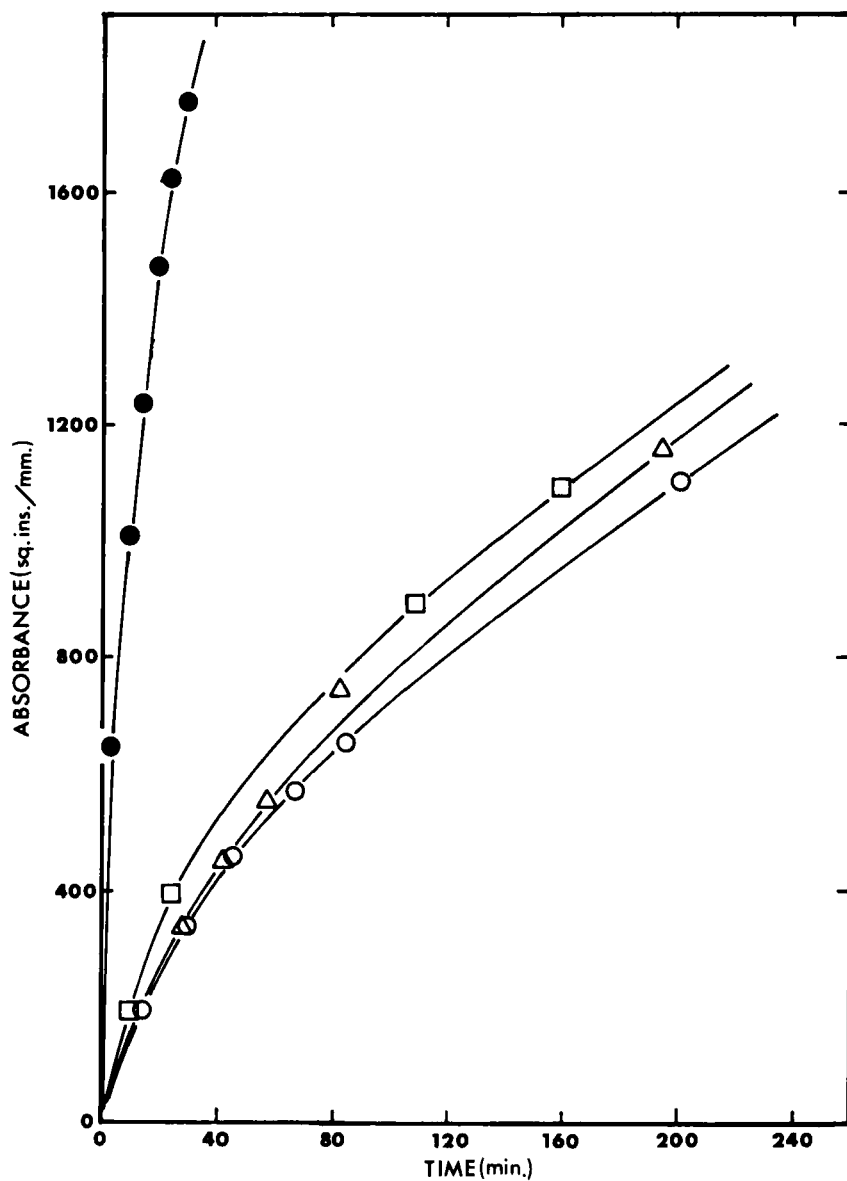


FIG. 5. Total visible (350-750 $m\mu$) absorbance vs time for radiation polymerized and commercial poly(vinyl chloride) films heated at 198°C in nitrogen: (○) commercial; (●) Sample B1; (△) Sample B5; (□) Sample B2.

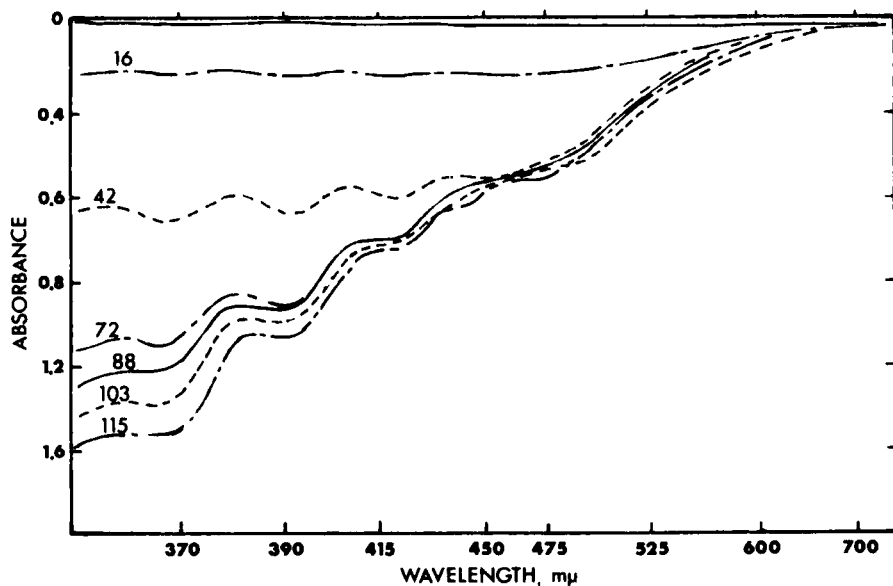


FIG. 6. Absorbance of radiation polymerized poly(vinyl chloride) (Sample B5) solution in ethyl benzoate at various times of heating at 198°C; numbers on spectra are minutes at 198°C.

DISCUSSION

Thermal Instability and Labile Structures

The radiation polymerized samples and exposed to the highest radiation doses, B1 and B6, are much less stable than the commercial PVC above 200°C, as shown in Table 2 and Figs. 5 and 7. On the other hand, the stability of Samples B2, B3, and B5, which had received less than 0.45 Mrad, is similar to the commercial PVC. In summary, the sequence of increasing stability is: B1, B6, B2, B4, B5, and commercial polymer. The stability sequence is in agreement with that of total dose which the samples had received during radiation polymerization except for the results of Samples B6 and B2 at 202°C in Table 2 and the commercial polymer in Fig. 7. However, Sample B6 polymerized at -78°C is more stable than B1 polymerized at 0°C, despite the former being exposed to much more dose than the latter. At present there is no available information to explain this discrepancy. The very low polymerization temperature and the resultant low reactivity of radical species may complicate the situation.

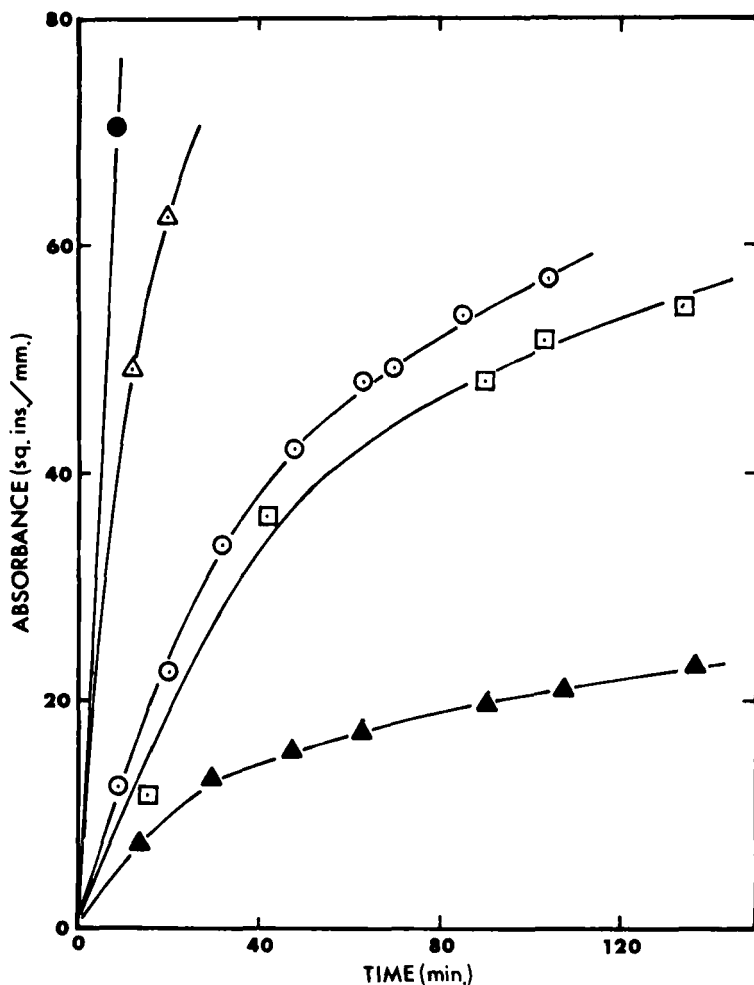


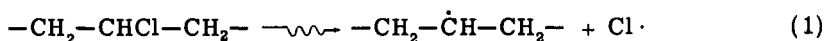
FIG. 7. Total visible (350-750 $m\mu$) absorbance vs time for radiation polymerized and commercial poly(vinyl chloride) solutions in ethyl benzoate heated at 198°C: (○) commercial; (●) Sample B1; (△) Sample B6; (◻) Sample B5; (▲) Sample B3.

The high thermal stability of model compounds of PVC such as 2,4-dichloropropane and 1,3,5-trichlorohexane confirms the view that the normal undisturbed PVC chain ($-\text{CH}_2-\text{CHCl}-$) is stable below 200°C [3, 12]. The instability of PVC could be derived from structural abnormalities in the PVC chains. The investigation of organic chlorine

compounds with structural irregularities shows that random isolated double bonds with allylic chlorine atoms or branches with tertiary chlorine atoms are thermally labile and responsible for the initiation of the thermal dehydrochlorination of PVC [11]. The role of unsaturated end groups as an initiation site for dehydrochlorination is not supported by the results of model compounds [11] and the oxidative cleavage measurements of heat-degraded polymers [14]. The contribution from chemical impurities such as chemical initiator is ruled out in the samples prepared by radiation bulk polymerization.

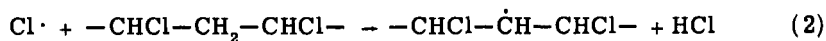
Since the dose dependency seems to indicate that the instability is derived from the irradiation of the resultant polymer chains during radiation polymerization, it is reasonable to assume that additional initiation sites of thermal dehydrochlorination are formed by the radiolysis of the resulting PVC chain.

On irradiation of bulk PVC at 77°K, trapped polymer radicals are formed, as shown by ESR measurements [15-17]. As the irradiated polymer is allowed to warm to room temperature, the primary radicals decay and are replaced by polyenyl radicals with the simultaneous liberation of hydrogen chloride and color formation [15-18]. During irradiation at room temperature, the polyenyl radicals are formed from both the initial stages and during post-irradiation storage at room temperature. The concentration of radicals is constant, however, although there is an increase in the concentration of conjugated double bonds [19]. From these results the propagation of radiation-induced dehydrochlorination has been accepted as proceeding via a free radical chain mechanism [6, 15-17]. The following mechanism of radiation-induced dehydrochlorination is essentially the same as that suggested by Miller [15]. The cleavage of the C-Cl bond and C-H bonds can lead to three possible primary polymer radicals: (A) $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$; (B) $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$; and (C) $-\text{CH}_2-\text{CCl}-\dot{\text{C}}\text{H}_2-$. The major primary radical process has been assumed to be the homolysis of the C-Cl bond to produce Radical A [15]:

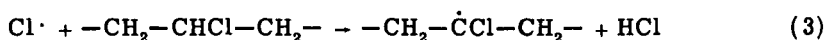


Radical A

This assumption is reasonable inasmuch as the C-Cl bond dissociation energy is about 20 kcal/mole less than that of either C-H bond, though the formation of hydrogen, $G(\text{H}_2) = 0.4$ [16], and the decay curve of the total radicals [8, 16, 18] suggests the presence of hydrogen atom cleavage. The homolysis of the C-Cl bond is followed by reactions of the chlorine atom as suggested by Winkler [13]:

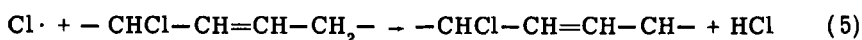
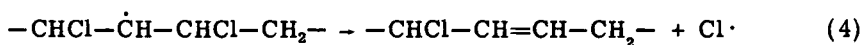


Radical B

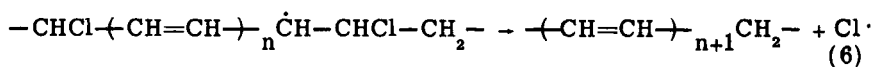


Radical C

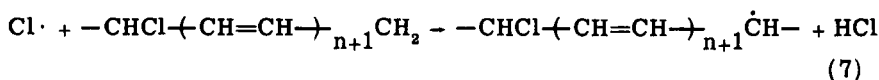
A distinction between Radicals B and C based on ESR analysis has not been made because of the smearing present in the initial spectrum. As Winkler [13] and Miller [15] point out, however, evidence from the free-radical chlorination of aliphatic chlorides and PVC suggests that abstraction of a methylene hydrogen to form Radical B (i.e., Reaction 2 is preferred. Radical B, in contrast to Radical A, is quite unstable and sustains the propagation of the chain reaction leading to the formation of HCl and conjugated unsaturation :



allyl radical



polyenyl radical



The resulting allyl and polyenyl radicals contain thermally-labile allylic chlorine atoms which remain even after radical termination.

In the radiation-induced bulk polymerization of vinyl chloride, the presence of vinyl chloride monomer does not seem to change greatly the primary process of the PVC radiolysis since the resulting polymer precipitates in the reaction medium. On the other hand, since monomers act as scavengers, the subsequent chain reaction of the dehydrochlorination (Reactions 2, 4, 5, 6, and 7) become competitive with the scavenging of the chlorine atoms and the polymer radicals by the monomer. The formation of the polyenes with long sequences is prohibited, as shown by no coloration of the radiation-polymerized samples. However, there is no available information about the extent of chlorine atom scavenging by the monomer. The recombination of polymer radicals (A, B, allyl, and polyenyl) and their reaction with the monomer can lead to branches and cross-links which contain only the thermally-stable branch sites with tertiary hydrogen atoms. The only precursor of the thermally-unstable branch site with tertiary chlorine atom is Radical C, which is a minor product in the radiolysis of PVC.

The presence of buried polymer radicals in the samples, resulting

from the heterogeneous polymerization, combining with oxygen to form peroxides (when the polymer is exposed to the air on opening the reaction ampoule) was tested. One of the ampoules prepared under identical reaction conditions was opened immediately after irradiation. Another ampoule was allowed to stand for a week in the dark at room temperature to terminate any buried radicals. It was found that, within experimental error, there was no difference in the stability of the polymers from the two ampoules. This result is supported by evidence [20] that trapped radicals were not observed by ESR measurements in the samples irradiated up to 60% conversion.

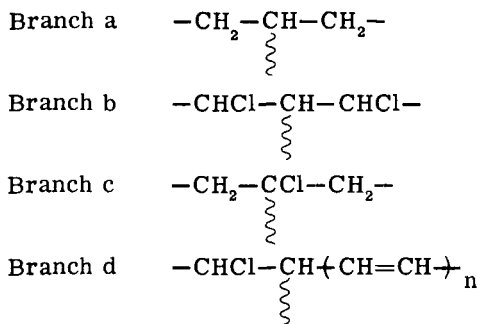
In conclusion, it appears that the allylic chloride groups produced by irradiation are mainly responsible for the thermal instability of radiation-polymerized PVC.

Effects of Branches on Thermal Stability

From Fig. 2 it can be seen that the weight loss of the commercial PVC is higher above 270°C than that of radiation-polymerized Samples B2 and B5. The isothermal TGA results in Table 2 also show that Sample B2 is more stable than the commercial PVC at 202°C, though the former is slightly less stable than the latter at 172 and 188°C. The better stability of radiation-polymerized samples was shown in the total visible absorbance measurements in ethyl benzoate solutions in Fig. 7, while those of the polymer films in Fig. 4 are somewhat different. It appears that the low dose samples show a lower rate of dehydrochlorination than the commercial PVC at relatively high temperatures.

This peculiar behavior seems to indicate that the propagation of dehydrochlorination in the radiation-polymerized samples is less than with the commercial PVC, whereas the initiation is higher than the latter as discussed previously. In other words, this may be explained in terms of the interruption of the propagation of dehydrochlorination along the polymer chain by structural irregularities such as branch points. As concluded above, the radiation-polymerized samples must contain additional unsaturations which cause the thermal instability. Furthermore, NMR analysis of a sample of radiation-polymerized PVC (Sample B7, precipitation polymerization in *t*-amyl alcohol solution) detected a significant concentration of chloromethyl groups, indicating that 5% of monomer units could be branch sites. Even if all the chain ends consist of chloromethyl groups, this figure is very high compared with PVC produced by other methods [21-24].

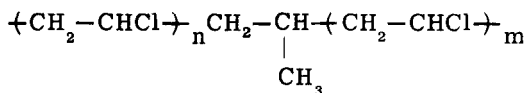
According to the possible polymer radicals produced in the PVC radiolysis, there are four possible branches which are formed from the radiolysis of the resulting polymer chains.



Since Radical A, which is a precursor of Branch a, is the major product in the radiolysis of PVC, Branch a probably is responsible for the high concentration of branches shown by NMR analysis.

Furthermore, regarding the efficiency of the interruption of the chain reaction, it would be completely terminated by Branch a and the unsaturations (including those with Branch d, if chain transfers of interrupted radicals to the other polymer chains do not occur).

On the other hand, Branches b and c may not interfere with the chain reaction, since they contain a chlorine atom at the α - or β -position which is necessary for the chain reaction. According to the above discussion, it is likely that the thermally-stable Branch a with a tertiary hydrogen atom accounts for the tendency which the low dose samples show. That is, a lower rate of dehydrochlorination compared with commercial PVC at relatively high temperatures. This conclusion is supported by the high thermal stability of vinyl chloride-propylene copolymers [25, 26]. The copolymer consists of isolated propylene units between relatively long sequences of vinyl chloride [25]. Since an isolated propylene unit



has the same structure as Branch a with respect to the main chain, the copolymer would seem to be ideal as a model polymer for examining the effect of the interruption of the propagation reaction by branching on the thermal stability of PVC. The thermal stability of vinyl chloride-propylene copolymers, prepared by a suspension polymerization process, was examined by the Brabender method at 190°C. A copolymer which contained about one unit for every 15 vinyl chloride units (4.7 wt% or 6.8 mole %) exhibited twice the stability of a PVC homopolymer [25, 26].

However, to propose the effect of the interruption by branch sites on the thermal stability of radiation-polymerized PVC, a more

systematic study of the correlation between the degree of branching, the dehydrochlorination rate, and the resultant polyene sequence would have to be carried out.

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