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Degradation of Poly(vinyl Chloride). II. Kinetic Investigation of Thermal and Radiation-Induced Polyene Formation at Low Temperatures

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Synopsis

The degradation arising from purely thermal treatments as well as with accompanying exposure to γ-radiation has been followed under vacuum by visible and ultraviolet spectroscopy in the temperature range from 80° to 130°C. As corroborated by extensive literature reports, absorbance changes have been considered suitable to provide valuable information on the unsaturation sequences produced. In agreement with the results obtained in the same conditions by following the evolution of HCl,[1] a catalytic action has been ascribed to HCl depending on the efficiency of removal of HCl. Furthermore, both the purely thermal and radiation-induced uncatalyzed degradations yield length distribution functions that are constant with time and have been found to be accounted for by the previously formulated free-radical mechanism, also from a quantitative point of view.

INTRODUCTION

The degradation process occurring in poly(vinyl chloride) (PVC) at temperatures from 80° to 130°C, both purely thermally and in combination with exposure to γ-rays, was dealt with previously[1] by following the evolution of HCl. The kinetic data could be accounted for plausibly by formulating in terms of the same mechanism both the thermal and radiation-induced processes under vacuum, although different mechanisms could not be excluded.

In this respect, an additional test can be provided by the investigation on the other degradation products, represented by the sequences of conjugated carbon–carbon double bonds left in the polymer chains, the relative abundance of the different unsaturation lengths being a parameter capable of discriminating among different kinetic models.

Analysis of degraded PVC for unsaturated structures was carried out chemically,[2,3] by infrared spectroscopy,[4–7] and by means of oxidation fol-

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lowed by oxygenated groups and/or molecular weight determination.[7–9] However, prevalent use was made of UV and visible light spectroscopy, by which unsaturation sequences are detectable with high sensitivity and, at least in principle, selectively.

Although in some cases the spectral changes were taken mainly as rough evaluations of the extent of degradation,[4,6,10–14] and in an effort to improve this use quantitative correlations with the amounts of split HCl were attempted,[9,15] mostly they were discussed in the light of the early recognized[16] possibility of matching degraded PVC spectra with the composite spectra of different polyene homologs mixed in convenient proportion.[3,11,14,16,29–54] By utilizing spectroscopy in the latter sense, comparative investigations of the thermally and radiation-induced degradation of PVC have been carried out in the temperature range from 80° to 130°C.

EXPERIMENTAL

Material

Commercial PVC, Sicron 548, was used without purification.

Tetrahydrofuran (THF), a RP C. Erba product, always maintained under N_2, was distilled first over NaOH after being refluxed 8 hr, and then over $LiAlH_4$, again after 8 hr of refluxing, followed immediately by use.

Procedure

Amounts of 0.6–0.7 g of polymer resin were introduced into 25-ml one-necked conical flasks of Pyrex glass, bearing a ⊤-shaped side tube closed at the lower end and sealed onto the flask neck at the other end. After evacuation at 10^{-5}–10^{-6} mm Hg by means of a vacuum line, the flasks were sealed off by flame at the neck. Then, taking care that the 3-cm-diameter flat bottom is homogeneously covered with thin layers of resin, the flasks were partially immersed in an oil thermostat regulated at the chosen temperature within 0.3°C. The side tube was kept cooled by liquid nitrogen to prevent the volatile products from coming into contact with the resin. At the end of the treatment times, 0.5 g of resin were recovered from each flask, crumbled into powder if aggregated into lumps, and added to 25 ml of THF under strong shaking to obtain complete dissolution in a few seconds. Absorption spectra of the solutions against THF as a reference were recorded in the 290–650 nm wavelength region by means of a double-beam Unicam SP 800 spectrophotometer, adopting silica cells of different path lengths according to the extent of discoloration.

In addition to this procedure, another one was also adopted, differing in that considerably larger amounts of resin were employed to form thick layers.

Finally, in a third procedure, besides using thick layers of resin, the volatiles pressures were allowed to increase freely in Pyrex glass vials, by which the flasks were replaced.

With the first procedure, runs were also performed with accompanying exposure to ^{60}Co γ-rays at a constant dose rate of 0.81 rad/sec, determined by means of a Fricke dosimeter, using $G(Fe^{3+}) = 15.6$.

RESULTS

For better correlating the present study based on the spectrophotometric analysis of degraded PVC dissolved in THF with the previous data[1] on the kinetics of HCl evolution, polymer from the same batch of commercial PVC was employed, again without purification. As before, degradation was confined to the very early stages, so that reactions of conjugation disruption, reported to take place during the treatment course,[7,30] could be safely disregarded.

The UV and visible light spectra were recorded with no delay after the instantaneous polymer resin dissolution in THF, accurately freed from peroxides, since in the THF solutions changes were established to occur on standing, in agreement with reported findings.[3,9,18] Conversely, no special notice was reserved for the time between the end of a run and the dissolution of the degraded polymer, storage of the latter as long as several months having little effect.

In spite of the very low degradation levels, very intense discolorations were attained, ranging from red to violet depending on treatment conditions. While with thin layers of resin and with volatile condensation by liquid nitrogen, i.e., the first procedure, degradation proceeded slower and yielded colors shifted toward the red, with thick layers of resin, i.e., the second procedure, and, still more, without volatile condensation, i.e., the third procedure, colors emerged faster and shifted toward the violet. Accordingly, in Figure 1 the corresponding absorption bands, from the shape of curve a, turned to the shape of curve b. Since HCl catalysis was operating under the conditions of the second and third procedures, as established previously by the accelerated evolution of HCl,[1] among its effects there should be an increase of light absorption preferentially at the longer wavelengths. For such a catalysis and the not unexpected poor reproducibility of the data it should be remembered, as before,[1] that the hindrance to the HCl diffusion and, therefore, its accumulation in the samples arise from the resin particles, which stick together in lumps in the course of the treatment and, occasionally, give rise to a sort of diaphragm. The latter event can account for the occurrence in certain cases of degraded samples exhibiting two colors, sharply separated by a cross-sectional boundary, with the lower layer strongly shifted toward the violet. Obviously, as witnessed by a slight appearance of double coloration, in some cases these effects could not be excluded to affect even the runs with the first procedure, owing to some accumulation of HCl even in thin layers of resin, especially when its production was enhanced by irradiation. As to the lowest temperatures investigated, where the changes in the resin's physical state were of minor importance, a different explanation should be undoubtedly formulated for

the observed pronounced shifting of the absorption bands toward the longer wavelengths, practically occurring to a similar extent with all procedures.

In this context it is worth comparing the absorption band observed in the presence of HCl with that typical of degradation in air[4,7,9,31,37] obtained with an open vial (curve b against curve c of Figure 1), from which the degradation acceleration operated by oxygen appears clearly to occur through a mechanism other than that due to HCl.

In the absence of oxygen, degradation of PVC yielded, as a rule, absorption bands exhibiting fairly well-resolved submaxima, except at 80°C, where resolution was poorer. By current views, if band shapes give general indications of the length of the unsaturation sequences produced[5,17–27] detailed information is to be gained by ascribing the absorptions around the wavelengths at which the submaxima lie (λ_{max}) to individual unsaturation lengths.[3,7,9,28–37]

By grouping the spectra according to whether they referred to degradations carried out thermally or with accompanying irradiation and, in the former case, further subdividing them on the basis of the procedure adopted to avoid HCl catalysis, the submaxima were found to lie in the wavelength ranges summarized in Table I. Together with them are also reported a series of λ_{max} found by other authors in widely different experimental conditions. Inspection of Table I reveals that virtual agreement exists within the λ_{max} values obtained here with each procedure; but a shift, slight but unaccountable by error in view of the number of spectra involved, is discernible when the procedure is changed. Analogous shifts can be observed among the literature data. It is noteworthy that the λ_{max} shifts toward the longer wavelengths increase as the treatment conditions increasingly favor HCl catalysis and, therefore, as the absorption bands of degraded PVC increasingly turn from curve a to curve b in Figure 1. Moreover, this seems to be the case also with the literature data.

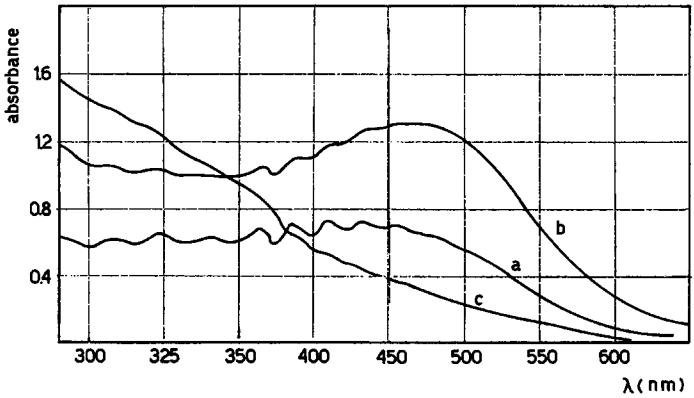

Fig. 1. Spectra of 1.5 g/l. solutions in THF of PVC thermally degraded: (a) and (b), 130°C, 30 hr with first and third procedure, respectively; (c), 120°C, 7 days in air. Optical path length = 1 cm.

TABLE I

λ_{max} Values in the Spectra of PVC Degraded Thermally and by Exposure to High-Energy Radiations[a]

Treatment conditions	λ_{max}, nm															
	$n = 1$	$n = 2$	$n = 3$	$n = (4)$	$n = 4$	$n = (5)$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$	$n = 10$	$n = 11$	$n = 12$	$n = 13$	ref.
1st procedure	—	—	—	—	303–05	318–21	333–37	359–62	380–83	404–07	427–32	448–53	467–70	490	510	this work
2nd procedure	—	—	—	—	305–08	321–23	336–42	361–66	383–88	410–14	431–38	452–58	472–78	—	—	this work
3rd procedure	—	—	—	—	304–05	320–25	336–42	363–68	385–90	412–18	435–40	456–60	473–78	493–500	—	this work
irrad.	—	—	—	—	305–07	320–22	335–38	360–63	382–85	406–10	428–32	450–54	468–70	482–88	510–14	this work
solut./salt	—	—	—	—	310	325	341	364	387	412	437	459	477	489	—	28
solut./KOH	—	240	274	285–86	306–10	321–25	336–40	364–66	386–88	410–14	434–36	452–58	474–80	—	—	30
powder	—	—	—	—	308	320	340	365	388	412	434	454	470	—	—	38
solut.	—	239	274	—	307	320[b]	337	363	385	409	429	440	468[b]	—	—	32
powder	—	—	—	286	312	326	346	369	394	420	445	466	486	—	—	9
powder	—	240	275	288	309	332	339	365	387	410	432	450	475	—	—	3
powder	—	—	—	—	308	320	340	365	388	412	434	454	470	—	—	37
solut.	—	—	—	286	—	317	334	350	378	405	432	460	—	—	—	35
film/pre-irrad.	244–50	290–91	330–32	—	368–73	—	400–04	430–35	460–72	485–87	510	530	—	—	—	39
film/pre-irrad.	—	—	329–30	—	364–65	—	400–05	430–35	458–60	483–85	505–10	—	—	—	—	19
film/pre-irrad.	250–52	285–91	330	—	369	—	—	—	—	—	—	—	—	—	—	27
models[d]	—	—	268	—	304[c]	—	334	364	390[c]	410	—	447	—	—	—	40
models[e]	—	—	257	—	290[c]	—	317	344	368[c]	386	—	420	—	—	—	40

[a] Treatment was thermal, except when specified otherwise.
[b] Approximately taken from Figure 12 of ref. 32.
[c] Interpolated from eq. (1).
[d] Peaks at longest wavelengths.
[e] Peaks next to longest wavelengths.

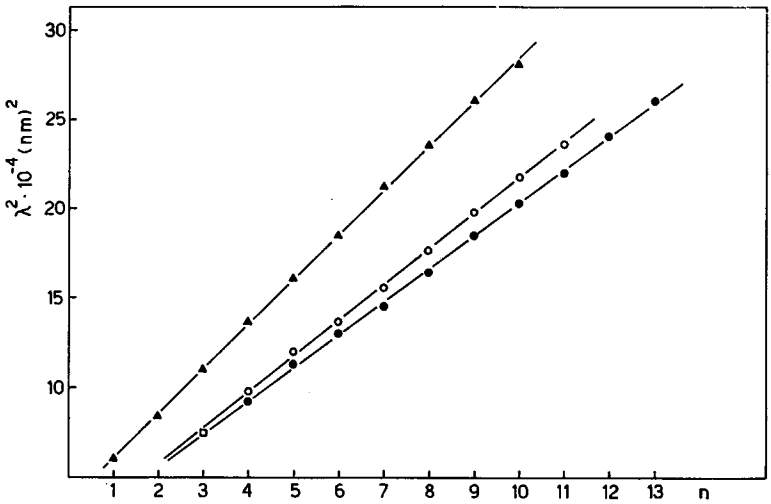

Fig. 2. Correlation between n and λ_{max}. Data of λ_{max} from Table I; rows corresponding to: (▲) ref. 39; (○) ref. 9; (●) this work, first procedure plus a point (□) from ref. 32.

In this context, the λ_{max} shifts observed here with accompanying irradiation in relation to those of purely thermal treatments can also be correlated with the spectrum shape modifications, already ascribed to some accumulation of HCl because of enhanced dehydrochlorination. At any rate, they differ considerably from the cases[19,26,27,39] of low-temperature degradation following preirradiation, where polyenyl radicals should be involved. In particular for the latter conditions, the λ_{max} values appeared to be more displaced from one another, as revealed by Table I and Figure 2.

These changes in λ_{max} do not seem to be perfectly in line with the view held by some workers[7,32,33,35,36] that polyene bands, though very broad and with various peaks, have only a peak at the longest wavelengths which, being far higher than any of the others, is capable of emerging from the degraded PVC spectrum to form a submaximum. Indeed, if this is to be rigorously maintained, λ_{max} values should not be liable to shift, owing to their implicit coincidence with the wavelengths of the peak of the polyene band. In a more realistic evaluation, the submaxima are considered by others[9,30] as largely affected by the extensive overlapping of the bands from polyenes of different lengths. On the other hand, the wavelengths of the band peaks of the higher polyene homologues do not appear to be such as to correlate too well with the number of conjugated double bonds n, applicable to the lower polyene homologues; and, consequently, the same should hold for the λ_{max} values in the degraded PVC spectrum. Thus, fitting the relationships formulated for the polyene homologues would appear to be rather fortuitous. As can be seen in Figure 2, the relationship[41]

$$\lambda_{max}^2 = kn \tag{1}$$

appears to be satisfied by both the λ_{max} series relative to the first procedure of this work; and one of the series of Table I shifted most considerably from it. Obviously, this applies to the other series in between. For the assessment of the n values to the λ_{max} values, for which there is some controversy, a convenient reasoning should be considered that has already been proposed by Bengough et al.[30] Two peaks in each polyene band are high enough to give rise to submaxima in the degraded PVC spectrum, specifically that lying more than any other toward the longer wavelengths is called "principal" and that next to it, "secondary." The wavelengths of these peaks can be conveniently taken from the data (also shown in Table I) found by Sondheimer et al.[40] for a number of low polyene homologues. Thus for each unsaturation length, two discrete submaxima should be present in the degraded PVC spectrum where polyene bands are sufficiently separated from one another. This is the case for n values equal to 4 and 5, where each one is given two λ_{max} values. In Table I, the λ_{max} values relative to "secondary" peaks are headed by n values in parenthesis. For n equal to 6, 7, and 8, the "secondary" peaks are largely superposed by the "principal" ones of the polyene homologues shorter by one double bond, and thereby they are no longer discernible. More arbitrarily, this superposition is also assumed to occur with the higher n values, with which the overlapping of polyene bands is more intriguing. This notwithstanding, the thus assessed n values, by which the submaxima can be denoted for simplicity's sake, permit approximate estimation of the length of unsaturation sequences.

Though with a still higher degree of arbitrariness, the degraded PVC spectrum is also susceptible of quantitative analysis. In fact, generally[7,32,33,35,36] this rests upon the absorbances at the λ_{max} values to be referred to the various n values giving the concentrations of all unsaturation lengths, i.e., the distribution function, when allowance is made for the absorbance contribution from neighboring unsaturation lengths merely by multiplying each absorbance by a constant empirical factor. Regarding this point, at any rate, it seems to be no objection to associate equal length distributions with degraded PVC spectra exhibiting equal absorbances, or differing in the same proportion, throughout all the wavelengths. This follows from the currently accepted[30,38] validity of the Lambert-Beer law in respect to the absorption of polyene species at low concentrations.

Spectra proportional in the above sense and, furthermore, exhibiting absorbances in linear relation with degradation time were generally obtained with samples pertaining to any single set of treatment conditions, when the first procedure with and without accompanying irradiation was adopted, as recognizable in the examples of Figure 3. This can be seen more directly if the results are reported as absorbance-versus-degradation time plots for all the λ_{max} values which, being evenly distributed, account properly for the spectrum as a whole. Such plots are shown in Figure 4 for the data of Figure 3 at some of the λ_{max} values, with the addition of the other points relative to the two sets of conditions under concern. As in Figure 4, straight lines could be drawn in general to reasonably represent

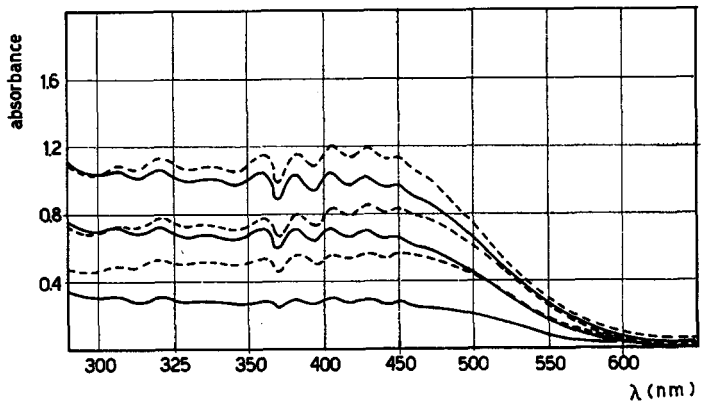

Fig. 3. Spectra of 2 g/l. solutions in THF of PVC degraded at 120°C with first procedure, purely thermally for 24, 63, and 88 hr (solid lines) and with accompanying irradiation for 29.5, 47, and 68 hr (dashed lines).

the kinetics of the absorbance changes, despite the noticeable scatter of the experimental points. The relative slopes, proportional to the rates of formation of various groups of unsaturation sequences (with proportionality factors varying with n), are shown in Table II for thermal degradation alone and in Table III for that with accompanying irradiation.

If this held for the treatments with the first procedure, though some tendency of the absorbance changes to accelerate was not to be absolutely

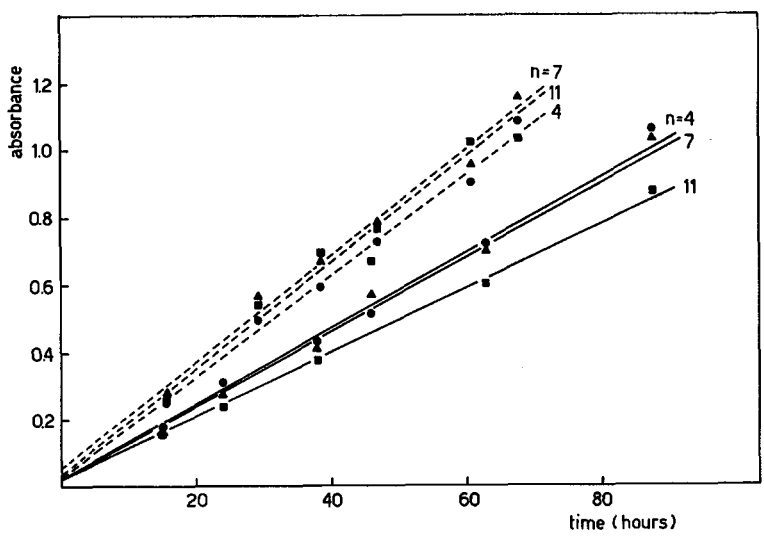

Fig. 4. Absorbance-vs.-time plots for degradation at 120°C, purely thermally (solid lines) and with accompanying irradiation (dashed lines). In both cases n values of 4, 7, and 11 refer to (●), (▲), and (■), respectively.

TABLE II

Slopes of Absorbance-Vs.-Time Curves in Thermal Degradation at Various n Values[a]

Temp., °C	Procedure	Slope × 10^7, sec^{-1}									
		$n = 4$	$n = (5)$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$	$n = 10$	$n = 11$	$n = 12$
80	1st	0.62	0.65	0.65	0.68	0.74	0.82	0.93	1.00	1.10	1.20
		(1)	(1.05)	(1.05)	(1.10)	(1.19)	(1.32)	(1.50)	(1.64)	(1.79)	(1.93)
	3rd	0.70	0.60	0.55	0.65	0.85	1.00	1.00	1.15	—	—
		(1)	(0.90)	(0.77)	(0.91)	(1.22)	(1.42)	(1.48)	(1.68)	—	—
90	2nd	3.0	3.0	2.7	2.7	2.7	3.1	2.7	3.7	3.7	—
		(1)	(1.00)	(0.90)	(0.90)	(0.90)	(1.03)	(0.90)	(1.23)	(1.23)	—
97	1st	3.2	2.8	3.1	3.3	3.2	4.0	4.4	4.7	4.5	—
		(1)	(0.87)	(0.97)	(1.03)	(1.00)	(1.25)	(1.37)	(1.47)	(1.41)	—
101	3rd	—	—	—	6.9	8.1	9.3	8.9	10.0	12.0	—
		—	—	—	(1)	(1.17)	(1.35)	(1.29)	(1.45)	(1.74)	—
110	1st	12.5	12.5	10.5	11.5	11.5	12.0	11.5	11.5	11.0	—
		(1)	(1.00)	(0.83)	(0.92)	(0.92)	(1.00)	(0.92)	(0.92)	(0.92)	—
	2nd and 3rd	—	13.0	13.0	15.0	15.0	17.0	19.0	21.0	22.0	—
		—	(1)	(1.00)	(1.15)	(1.15)	(1.31)	(1.46)	(1.61)	(1.69)	—
120	1st	29.0	29.0	28.0	29.0	29.0	29.0	28.0	27.0	24.0	—
		(1)	(1.00)	(0.96)	(1.00)	(1.00)	(1.00)	(0.96)	(0.93)	(0.83)	—
	2nd and 3rd	30.0	32.0	34.0	33.0	36.0	38.0	30.0	35.0	38.0	—
		(1)	(1.07)	(1.13)	(1.10)	(1.20)	(1.27)	(1.00)	(1.17)	(1.27)	—
130	1st	74	74	66	71	71	71	63	59	50	—
		(1)	(1.00)	(0.89)	(0.96)	(0.96)	(0.96)	(0.85)	(0.80)	(0.67)	—
	2nd	85	95	95	85	90	100	85	80	70	—
		(1)	(1.10)	(1.13)	(0.99)	(1.07)	(1.15)	(1.01)	(0.92)	(0.81)	—

[a] For second and third procedures, taken from initial curves. Values in parentheses are slope ratios.

TABLE III
Slopes of Absorbance-Vs.-Time Curves at Various n Values[a]

Temp., °C	Slope × 10^7, sec^{-1}										
	n = 4	(5)	5	6	7	8	9	10	11	12	13
80	28	31	31	34	32	35	44	50	56	62	66
	(1)	(1.10)	(1.10)	(1.20)	(1.10)	(1.20)	(1.60)	(1.80)	(2.00)	(2.20)	(2.40)
	0.62	0.50	0.61	0.54	0.48	0.77	0.91	1.00	1.07	1.20	—
	27.4	30.5	30.4	33.5	31.5	34.2	43.1	49.0	54.9	60.8	—
90	16	17	18	23	26	31	36	41	48	54	58
	(1)	(1.10)	(1.10)	(1.40)	(1.60)	(1.90)	(2.20)	(2.60)	(3.00)	(3.40)	(3.60)
	1.8	1.5	1.7	1.6	1.5	2.1	2.3	2.4	2.5	—	—
	14	15	16	21	24	29	34	39	45	—	—
97	23	23	19	23	23	25	32	34	38	41	—
	(1)	(1.00)	(0.80)	(1.00)	(1.00)	(1.10)	(1.40)	(1.50)	(1.60)	(1.80)	—
	3.6	3.2	3.5	3.3	3.2	4.1	4.4	4.5	4.4	—	—
	19	20	15	20	20	21	28	29	34	—	—
110	25	25	24	25	27	29	32	33	33	33	—
	(1)	(1.00)	(1.00)	(1.00)	(1.10)	(1.10)	(1.30)	(1.30)	(1.30)	(1.30)	—
	12.5	12.0	11.5	11.5	11.5	13.0	13.0	12.5	11.5	—	—
	12.5	13.0	12.5	13.5	15.5	16.0	19.0	20.5	21.5	—	—
120	36	39	37	39	41	43	42	43	42	—	—
	(1)	(1.10)	(1.00)	(1.10)	(1.10)	(1.20)	(1.20)	(1.20)	(1.20)	—	—
	30	30	27	29	29	30	28	27	24	—	—
	6	9	10	10	12	13	14	16	18	—	—
130	90	90	90	97	97	97	86	86	86	86	—
	(1)	(1.00)	(1.00)	(1.10)	(1.10)	(1.10)	(0.90)	(0.90)	(0.90)	(0.90)	—
	73	75	64	71	75	70	63	58	48	—	—
	17	15	26	26	22	27	23	28	38	—	—

[a] First row: in degradation with accompanying irradiation; second row: ratios of slopes in first row; third row: from Arrhenius plots of thermal degradation data; fourth row: slope increments due to irradiation.

excluded, conversely with the second and still more with the third procedure, the absorbance-versus-degradation time plots exhibited accelerations increasing with degradation time and with temperature in the same pattern as ascertained by following the HCl evolution.[1] Furthermore, scattering was markedly broader, in line with the much greater anomalies observed in discoloration behavior. Since the kinetic curves could be drawn only with some degree of arbitrariness, initial slopes could be derived only as crude estimates. The latter, averaged from the second and third procedures, appear to approach the slopes obtained in the continuous removal of HCl, in agreement with the fact that initially there is not yet an important accumulation of HCl (see Table II). However, as observed in previous investigations,[1] this approach becomes worse the higher the temperature.

Besides, it appears that there is an increasing divergence in the slopes obtained from different procedures as progressively increasing n values are concerned. To reveal the latter pattern, relative values of the slopes with respect to that at the lowest n can be more suitable, as shown in Tables II and III. This implies that the progressive divergence of the kinetic curves due to HCl catalysis takes place more rapidly the larger n is, in agreement with the fact that an overall absorption maximum at the longer wavelengths is observed in the relative spectra at the later stages. On the other hand, the kinetic data relative to the first procedure show that a shift of the length distribution toward the longer unsaturation sequences occurs with decreasing temperature, as observed in a range of higher temperatures.[7,9,31] More directly, this trend could be disclosed by determining the temperature coefficients of the slopes at the various n values. As can be seen from the Arrhenius plots relative to the n values of 4, 8, and 11 of Figure 5, alignments of the points better than expected, given the poor reproducibility of the measurements, were found almost in every case, so that straight lines slightly differing in slopes could be confidently traced. The determined activation energies appeared to range from 28 to 26 kcal/mole as n changes from 4 to 8 and to fall more notably to 24, 23, and 22 kcal/mole at n values of 9, 10, and 11, respectively. As to the unavailable data for the shortest polyenes, is seemed justified to extend also to them the pattern of the continuous rising in activation energy as n diminishes, at least on the grounds that no arguments pointing to a discontinuity in behavior could be conceived.

Since the activation energies appear to be comprised within a comparatively narrow range, the activation energy for the total HCl loss reaction should lie within this range, or at least not far from it. These results, therefore, are in good agreement with the dehydrochlorination activation energy of 28 kcal/mole which was determined previously.[1]

Shifts toward the longer unsaturation sequences similar in extent (apart from the temperatures of 80° and 90°C) to those exhibited from the initial slopes of accelerated kinetic curves can be deduced from the data in Table III for degradation with accompanying irradiation. This pattern could be explained by the catalytic action of HCl, which accumulated in the

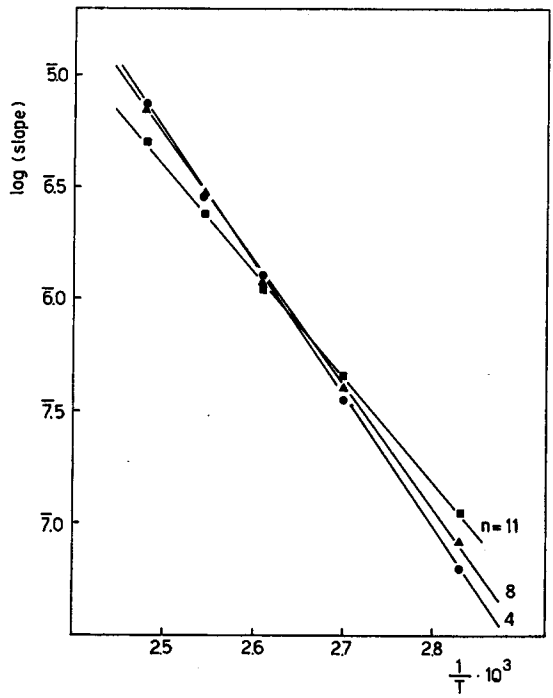

Fig. 5 Arrhenius diagrams of the slopes of absorbance-vs.-time plots for thermal degradation. The relative n value is shown on each curve.

sample in amounts similar to those of the initial stages of the accelerated kinetics, when its production was enhanced by irradiation.

By subtracting the absorbance change rates for the purely thermal degradation, as derived from the Arrhenius plots, from the composite rates, the increments in rate attributable to the irradiation action were obtained. From examination of Table III, where they are reported, no systematic change with temperature can be observed and, though the scattering is appreciably broader than that found with the increments in HCl evolution rate due to irradiation,[1] the same conclusion of temperature independence is not unreasonable. The agreement, furthermore, can be extended to include also the quantitative aspect, in that the increments in rate produced by the same dose rate at the various temperatures range in both cases between the rates at 110° and those at 120°C.

DISCUSSION

Inasmuch as the split off HCl evolving from degraded PVC and the unsaturation sequences left in the polymer are the products of one process, the kinetic features of the unsaturation formation should parallel those encountered in the evolution of the volatiles. Indeed, in common with the previous investigation on the kinetics of the latter,[1] the present results show

that an accelerating influence is exerted by HCl present in the atmosphere or accumulating in the polymer sample, and that, by improving the efficiency of the continuous gas removal, the rates tend to remain constant at their initial values.

From a more quantitative point of view, an agreement also exists in the length of time the rates take to double or treble in the HCl-catalyzed degradation and, when catalysis is avoided, in the rate dependence on temperature and in the proportion of the rate contributions due to irradiation.

In addition, valuable information is provided for proposing a degradation mechanism and with reference to which the previously reported mechanism actually proposed.[1]

The finding of degradation products, which not only consist of a rather broad distribution of unsaturation sequences from the beginning, as generally admitted, but also, when HCl is efficiently removed, exhibit constant length distribution while total unsaturation increases linearly with time, can be accounted for readily by a chain reaction in which stationary-state conditions apply to the active centers. Beside the identification of the latter with the free radicals, specifically, as generally accepted, Cl atoms which, by abstracting methylene H atoms, transform into polymer radicals, from which double bonds originate by loss of adjacent Cl atoms (see the review by Geddes[42]), the previous data[1] led to a rate of formation of double bonds or of HCl evolution expressed as

$$R_p = KR_i \tag{2}$$

where R_i is the rate of free-radical production and K is a constant, assuming constant concentrations of reacting species together with a temperature-independent ratio of rate constants. A crude estimation of K, which corresponds to the number of double bonds formed per propagating radical, led to a value of 36. In this respect, the experimental evidence of a much shorter average length of unsaturation sequences can be accounted for by the assumption[1] of Cl atoms attacking not only adjacent methylene groups to form single unsaturation sequences, but also other methylene groups to start new sequences. Also, by the change in the relative frequency of these two types of propagation reaction, the slight temperature dependence of the unsaturation distribution may be accounted for without invalidating the temperature independence of K. An alternative explanation, however, may be a somewhat increasing hindrance to HCl diffusion to be imputed to the unmodified resin particles as the 80°C temperature is approached.

By this, it can be also explained, bearing in mind the important degradation contribution due to accompanying irradiation, why the latter at the lowest temperatures investigated yields rather pronounced shifts in length distribution toward the longer unsaturation sequences. At the other temperatures, these shifts appear to reduce to extents similar to those occurring in the initial stages of the accelerated thermal degradation; therefore, they can be attributed to catalysis by HCl which, because of its enhanced production, accumulates in similar amounts. In other words, if the HCl catal-

ysis could be avoided, purely thermally length distribution functions should be considered not to differ from those relative to radiation-induced degradation. This is of relevance in that it justifies the conclusions previously reached[1] by assuming the kinetic scheme leading to eq. (2) to apply to both cases with the same rate constants. In fact, by the kinetic scheme based on a first-order reaction of deactivation of the chain reaction active centers, unsaturation sequences will have their lengths regulated by the relative frequencies of the deactivation reaction and the propagation steps, independently of the active centers concentration and, thereby, of the initiation rate R_i. Therefore, equality of length distributions is to be taken as strongly, though not unequivocally, pointing out to an identity of the rate constants.

In this way, obviously, the active centers are identified by the free radicals, in view of the general acceptance of a free-radical mechanism in radiation-induced degradation. In this respect it is worth mentioning recent evidence[25–27] supporting the previously proposed mechanism.[1] It has been provided by following, at very low temperatures, the slow transformation of the radiolysis-produced alkyl radicals into polyenyl radicals progressively longer, i.e., allyl dienyl, trienyl, etc., and by ascertaining the occurrence at less low temperatures of transfer reactions by which polyenyl radicals cease to grow and alkyl radicals are regenerated. In addition, by inference of polyenyl radicals undergoing no disappearance but a deactivation when they become too long before a transfer reaction takes place, an alternative way is provided to explain the rather unsettled point[1] of the first-order radicals termination. A similar destiny of no destruction but of persistence in an immobilized matrix has also been assigned to thermally generated polyenyl radicals either below a limiting concentration[43] or with no limitation in concentration.[44]

Before concluding that the here gathered evidence is definitely in favor of a free-radical mechanism operating in the thermal PVC degradation, the discussion should also involve the HCl catalysis, generally taken as an argument for a different interpretation. In this respect, it should be borne in mind that the reaction mechanism in thermal PVC degradation is a still controversial issue, despite literature on the subject amounting to some 500 papers. (Very recently there also have appeared papers both against[7,45–48] and in favor[43,44,49–51] of a free-radical mechanism.)

Mechanisms of nonradical nature are based on the greater ease by which HCl is split off when allylic chlorine atoms rather than normal ones are involved, as deducible from the behavior of model compounds.[45–47] Consequently, since with normal head-to-tail PVC structures allylic activation is restored after any loss of HCl, a rapid zipper-like dehydrochlorination will result once a macromolecular chain is provided with one of the unsaturation groupings capable of sufficiently activating adjacent C–Cl bonds, such as a single double bond, if not located at the chain end[7,45–47] and, more specifically, if being the cis isomer.[46] As a corollary of this formulation, moreover, the ease with which PVC undergoes dehydrochlorination is currently

ascribed to the above active unsaturation groupings either already present in the polymer or being generated by other anomalous structures (see review of refs. 42 and 47) and even by normal structures.[35]

Apart from the first hypothesis, by which simultaneous lengthening of all unsaturation sequences would be expected, the experimental evidence can be accounted for if, besides a slow creation of the active unsaturation groupings, the occurrence of the zip-dehydrochlorination termination can be postulated. For the latter, chain irregularities, making the allylic activation fail to be restored, can be most convincingly invoked; and, using a mathematical model, kinetic equations fitting an experimental behavior similar to that observed here could be derived.[35] In relation to the overwhelming production of short unsaturation sequences, however, an unrealistic number of irregularities would be required. Furthermore, no accommodation can be provided for the changes occurring in length distribution with the variations in treatment conditions, for instance, when HCl catalysis set in.

In this context, it is worth mentioning that if for the degradation of PVC in solution (apart from the cases of particularly reactive solvents[30,31]) evidence both favoring[7,32] and opposing[30,36] HCl catalysis is to be recorded, in bulk degradation, however, no such an uncertainty exists. Data[49,52–55] proving the catalytic action of HCl continue to accumulate, in addition to those collected as references in the previous work.[1] As to the lengthening of the unsaturation sequences, too, literature reports[7,22] appear to agree with the present findings. In the interpretation of this action, an interaction of HCl with the degrading PVC macromolecules of ionic character is currently[7,22,32] suggested. In support for it is the observation that a number of chlorides of metal and of polyatomic cations exhibit an accelerating influence on the degradation in bulk[22,56] and in solution,[32,57] and in special solutions very pronouncedly so.[28,30,31] Recently,[48] the ionic character of HCl in degrading PVC has been associated with the formation of the $(\text{polyene}\cdots\text{H})^+\ \text{Cl}^-$ complex, whose existence has been suggested[13,47] to account for most of the discoloration in bulk degraded PVC.

As to the common practice of extending the same mechanism to the uncatalyzed reaction, it should be remembered that, much in the same way, a free-radical mechanism may be derived by such a mechanism being proposed[42,47] for the oxygen interaction with degrading PVC on the basis of the recognized reaction properties of the O_2 molecule. Therefore, apart from the fact that in a picture of a degradation occurring via free radicals, an explanation of the HCl action may be formulated in terms of a free-radical mechanism with some degree of plausibility[55,58] also, the more acceptable ionic catalysis should not be considered to necessarily invalidate the here proposed kinetic scheme. On the other hand, with it, an accommodation to concurrent degradation reactions, even of ionic mechanism leading to longer unsaturation sequences, is allowed with less embarrassment than with the allylic activation mechanism, owing to the absence of any unsaturation length predetermination by chain irregularities.

To this point, it should be mentioned that just the ionic-catalyzed degradation of PVC in special solutions, where lengths of unsaturation sequences range around 13–16 double bonds, presumably allows the zipper dehydrochlorination to proceed along the chain to the farthest distance compatible with macromolecular structure.[31]

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