Table III
Calculated f for $(Ala_4ArgAla_5)_x(Ala_5ArgAla_4)_x$[a]

x	water	0.006 M $NaDodSO_4$
1	0.087	0.109
2	0.332	0.319
3	0.526	0.457

[a] 25 °C; the values of σ and s are 8×10^{-4} and 1.07 for Ala in both solvents. For Arg, they are 1×10^{-5} and 1.03 in water and 0.01 and 0.82 in $NaDodSO_4$.

Table III presents values of f calculated for copoly(amino acids) of defined sequence in which 10% of the residues are Arg and 90% are Ala. Ala is chosen here as an example of a nonionic residue with a small σ and $s > 1$. A change in the vaues of σ and s for Arg from those determined previously[16] in water to the current results in 0.006 M $NaDodSO_4$ produces a decrease in helix content if the degree of polymerization is large. The change is easily rationalized by the decrease in s for Arg. However, the same parameters predict an increase in helix content at sufficiently small degree of polymerization, as shown by the entries with $x = 1$ in Table III. Rationalization of this observation must focus on the change in σ. If helices are short (and they must be short if the degree of polymerization is small), there is no opportunity for recovery from the penalty reflected by an extremely small value of σ. Insertion of a residue with a comparatively large σ will then enhance the helix content (even if s is small), because it means that the penalty accompanying helix initiation can be overcome by an attainable number of propagation events.

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Registry No. $NaDodSO_4$, 151-21-3; (L-arginine)(hydroxybutyl L-glutamine) (copolymer), 111189-12-9.

References and Notes

(1) McCord, R. W.; Blakeney, E. W., Jr.; Mattice, W. L. *Biopolymers* **1977**, *16*, 1319.
(2) Grourke, M. J.; Gibbs, J. H. *Biopolymers* **1967**, *5*, 586.
(3) Satake, I.; Yang, J. T. *Biochem. Biophys. Res. Commun.* **1973**, *54*, 930.
(4) Sarkar, P. K.; Doty, P. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *55*, 981.
(5) Li, L.; Spector, A. *J. Am. Chem. Soc.* **1969**, *91*, 220.
(6) Mattice, W. L.; Harrison, W. H., III *Biopolymers* **1976**, *15*, 559.
(7) Igou, D. K.; Lo, J. T.; Clark, D. S.; Mattice, W. L.; Younathan, E. S. *Biochem. Biophys. Res. Commun.* **1974**, *60*, 140.
(8) Overgaard, T.; Erie, D.; Darsey, J. A.; Mattice, W. L. *Biopolymers* **1984**, *23*, 1595.
(9) Zimm, B. H.; Bragg, J. K. *J. Chem. Phys.* **1959**, *31*, 526.
(10) Kubota, S.; Ikeda, K.; Yang, J. T. *Biopolymers* **1983**, *22*, 2219.
(11) Kubota, S.; Ikeda, K.; Yang, J. T. *Biopolymers* **1983**, *22*, 2237.
(12) Wu, C.-S. C.; Yang, J. T. *Biochem. Biophys. Res. Commun.* **1978**, *82*, 85.
(13) Robinson, R. M.; Blakeney, E. W.; Mattice, W. L. *Biopolymers* **1982**, *21*, 1217.
(14) von Dreele, P. H.; Poland, D.; Scheraga, H. A. *Macromolecules* **1971**, *4*, 396.
(15) von Dreele, P. H.; Lotan, N.; Ananthanarayanan, S.; Andreatta, R. H.; Poland, D.; Scheraga, H. A. *Macromolecules* **1971**, *4*, 408.
(16) Konishi, Y.; van Nispen, J. W.; Davenport, G.; Scheraga, H. A. *Macromolecules* **1977**, *10*, 1264.
(17) Van Nispen, J. W.; Hill, D. J.; Scheraga, H. A. *Biopolymers* **1977**, *16*, 1587.
(18) Hill, D. J.; Cardinaux, F.; Scheraga, H. A. *Biopolymers* **1977**, *16*, 2447.
(19) Archibald, W. J. *J. Phys. Colloid Chem.* **1947**, *51*, 1204.
(20) Klainer, S. M.; Kegeles, G. J. *J. Phys. Chem.* **1955**, *59*, 952.
(21) Williams, J. W. *Ultracentrifugation of Macromolecules*; Academic: New York, 1972; Chapter 1.
(22) Schachman, H. K. In *Methods of Enzymology*; Colowick, S. P., Kaplan, N. O., Eds.; Academic: New York, 1959; Chapter 1.
(23) Yphantis, D. A.; Waugh, D. F. *J. Phys. Chem.* **1956**, *60*, 623.
(24) Lin, T. H.; Cherry, W. R.; Mattice, W. L. *Polymer Commun.* **1986**, *27*, 3.
(25) Mattice, W. L. *Biopolymers* **1974**, *13*, 169.
(26) Greenfield, N.; Fasman, G. D. *Biochemistry* **1969**, *8*, 4108.
(27) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapters 7, 14.
(28) Scheraga, H. A.; Mandelkern, L. *J. Am. Chem. Soc.* **1953**, *75*, 179.
(29) Emerson, M. F.; Holtzer, A. *J. Phys. Chem.* **1965**, *69*, 3718.
(30) Emerson, M. F.; Holtzer, A. *J. Phys. Chem.* **1967**, *71*, 1898.

Catalytic Effect of HCl on the Dehydrochlorination of Poly(vinyl chloride)

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ABSTRACT: Two poly(vinyl chloride) (PVC) samples with different thermal stability were degraded in both pure nitrogen and in an atmosphere containing HCl. The degradation experiments were made in a thermogravimetric system where the weight loss was measured. The polyene sequence distributions were monitored by UV-visible spectroscopy and the increase in the number of polyene sequences during degradation was measured by ozonolysis. The PVC sample with increased thermal stability showed less severe discoloration, i.e., the polyene sequences were shorter, when degraded in pure nitrogen. On the other hand when degradation was performed in an atmosphere containing HCl both the rate of dehydrochlorination and the polyene sequence length increased. For the PVC with normal thermal stability there was no measurable difference in either the dehydrochlorination rate or the length of the polyene sequences for degradation in nitrogen compared with degradation in HCl. From these results we have suggested a mechanism for the HCl catalysis of the propagation step in the degradation of PVC, which is based on an ion-pair mechanism. Due to the presence of HCl the equilibrium is shifted to form more ion pairs and the HCl "stabilizes" the cation, thus leading to the chloride ion being nearer the end of the sequence and more able to abstract the methylene proton.

Introduction

In thermal degradation of PVC, dehydrochlorination is the dominating reaction. In earlier investigations we have been able to correlate the amount of labile chlorine to the dehydrochlorination rate.[1-3] According to these results tertiary chlorine is the most important defect, since it is much more frequent than the internal allylic chlorine. In agreement with other published reports,[4-7] we have found

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Table I
Data of Investigated Polymers

sample	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_w M_n$	$[\eta]$
A	46	109	2.4	0.92
B	46	115	2.5	0.91

evidence that the normal PVC units are unstable at the temperature in question, i.e., random initation will occur. We have used this knowledge to produce a PVC with improved thermal stability. The degradation rate for this PVC is reduced to about 40% of a commercial PVC.

During the degradation of the improved PVC we realized that not only the dehydrochlorination rate was decreased but also the discoloration was less severe.[8] This phenomenon has also been reported by others,[9-11] who have used different methods to achieve more thermostable PVC, e.g., substitution with Et_3Al[9] or anionical polymerization.[8] In all these cases the common factor is the reduced rate of dehydrochlorination, which results in a lower concentration of HCl in the sample. This affects the length of the polyenes, i.e., the discoloration. In our previous paper[8] we discussed different possibilities for HCl to influence the length of the polyenes. The most probable alternative was for HCl to catalyze the elongation of the polyenes.

We have studied the degradation behavior for samples degraded in pure nitrogen compared with samples degraded in an atmosphere with added HCl. We have used both normal PVC and PVC with improved thermal stability. Our results have enabled us to suggest a mechanism for the HCl catalysis of the propagation step.

Experimental Section

PVC Samples. Two types of PVC, sample A and B, have been used in this investigation. Both samples were obtained by suspension polymerization at 56 °C in a 5-L stainless steel reactor. Poly(vinyl alcohol) was used as the suspending agent and dicetyl peroxydicarbonate as the initiator. Vinyl chloride of polymerization grade was supplied by Norsk Hydro Plast AB, Sweden. After water had been charged, air was removed by five cycles of evacuation and purging with extra pure nitrogen (<2 ppm O_2). All additions were made under a nitrogen blanket. The polymerization was stopped shortly after the pressure drop. In the polymerization of sample B a small amount (0.1%) dibutyltin ester was added to the vinyl chloride before the polymerization according to ref 12 and 13, in order to substitute labile chlorine. The following transformation might therefore have occurred:

$$\sim C{=}CC(Cl)\sim \longrightarrow \sim C{=}CC(OC(=O)R) \quad (1)$$

Molecular weight data determined by GPC and viscometry are given in Table I for both samples.

Thermal Degradation. Thermal degradation experiments were performed with two different types of apparatus. A Perkin-Elmer TGS-2 was used to measure the weight loss of the PVC samples during degradation in a pure nitrogen atmosphere (<5 ppm O_2) and in HCl/nitrogen atmosphere (15% HCl). The heating rate was 320 °C/min up to 190 °C where the temperature was held constant. The sample weight was about 10 mg. Degradations were also performed in a specially designed apparatus.[14] Bulk samples (150 mg) were heated at 190 °C in either nitrogen (<5 ppm O_2) or HCl/nitrogen (15% HCl) atmospheres. The dehydrochlorination was followed conductometrically when nitrogen atmosphere was used. In the case of an atmosphere containing HCl the degradation time to a certain degree of dehydrochlorination was calculated from the degradation rate obtained in the TGS experiments. For both techniques the rates of dehydrochlorination are expressed as evolved HCl, as a percentage of the theoretical amount, per minute.

Molecular Weight Distribution. Gel permeation chromatography (GPC) and viscometry were used to determine the molecular weight distribution, MWD. Details of the GPC analysis and dissolution procedure have been given earlier.[15] A Waters Associated GPC Model 200 operating at 25 °C with tetrahydrofuran (THF) as solvent was used for the process. The column combination consisted of five Styragel columns with permeabilities ranging from 10^3 to 10^7 Å, which enabled good separation in the molecular weight range of interest. The setup also contained a SEPEMA on-line viscometer. The viscometer is of the Ubbelohde type and includes a syphon with a volume of 4.57 mL (V_s). The effluent time of pure solvent (t_0) was 113.75 s. The variation in t_0 was less than ±0.01 s. The intrinsic viscosity ($[\eta]$) was calculated according to

$$[\eta] = \frac{\sum \Delta t V_s}{t_0 c_0 V_i} \quad (2)$$

where Δt is the time difference between solution and pure solvent for each fraction, c_0 is the concentration of polymer in the injected solution, and V_i the injected volume.

To calculate MWD and molecular weight averages the computer program devised by Drott and Mendelsson[16] was used, assuming trifunctional branch points. The calibration for linear PVC was obtained via the universal calibration curve as described earlier.[15]

Polyene Sequence Distribution. The polyene sequence distributions in the degraded samples were determined qualitatively by UV–visible spectroscopy. The absorbance spectra were obtained from tetrahydrofuran solutions with a Perkin-Elmer 554 spectrophotometer. The solutions (4 g/L) were carefully prepared under nitrogen using peroxide-free THF.[15]

Internal Double Bonds. The number of internal double bonds (or sequences) was determined by following the changes in M_n caused by the ozone oxidative cleavage of all double bonds. The ozonolysis was performed principally according to Michel et al.[17] PVC (500 mg) was dissolved in cyclohexanone (100 mL) and a small amount of methanol was added to facilitate the cleavage of the newly formed ozonide. The ozonolysis was performed at −20 °C for 2 h and the polymer was recovered by precipitation in methanol and vacuum dried for 24 h. The number of internal cleavages per 1000 monomer units ($(C = C_n)/1000VC$) was calculated from the number-average molecular weight before ($M_{n,0}$) and after (M_n) oxidative treatment:

$$C = C_{int}/1000VC = (1/M_n - 1/M_{n,0})62500 \quad (3)$$

Results

In dehydrochlorination experiments, evolved HCl is usually measured conductometrically or by titration. Adding HCl in the carrier gas results in neither of these methods being of use. Instead we have used, for the introductory experiments, a thermogravimetric system (TG) where the weight loss is measured. To obtain the same rate of dehydrochlorination for sample A in a nitrogen atmosphere in the TG as in our ordinary apparatus (OA) at 190 °C, we had to adjust the temperature to 192 °C in the TG. This temperature difference is due to many factors, e.g., the precision of the thermoelements, different heat transfer conditions, etc.

A typical weight loss curve is illustrated in Figure 1. Before the experiments we heated the PVC samples to 80 °C to eliminate water, held the temperature constant until the weight loss was almost zero, and then cooled the samples to room temperature. In spite of this some water loss was still observed in the beginning of the experiments. Thereafter the weight loss became linear. From the linear part of the degradation curve we have extrapolated to the start of degradation, which is the time when the sample reaches 190 °C. We have assumed all the weight loss to be HCl, since HCl is the dominating volatile component produced at the temperature in question.[18]

If we compare this curve with a degradation curve from the OA, Figure 2, we realize that in the TG there is no detectable induction period. The induction period is consequently just an apparatus constant. In the TG we use a small sample of 10 mg, which is 15 times less than in the OA, the heating rate is rapid, and the dead volume

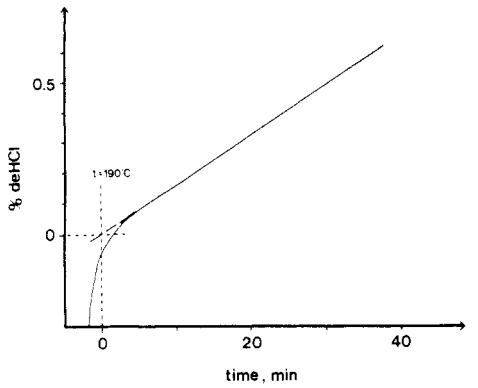


Figure 1. Degradation curve from the TG for sample A degraded in nitrogen. The degradation time starts when the temperature reaches 190 °C. The dehydrochlorination is extrapolated from the linear part to the start of the degradation time where the evolved HCl is zero.

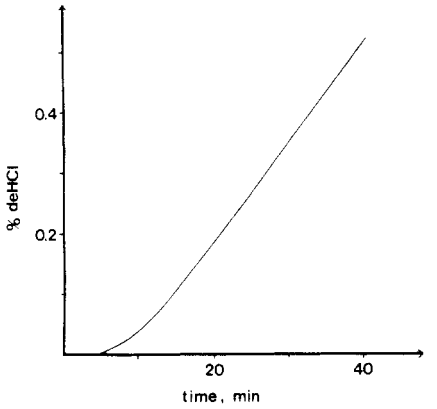


Figure 2. Degradation curve from the OA for sample A degraded in nitrogen at 190 °C.

Table II
Dehydrochlorination Rate at 190 °C

	%deCHl/min × 10^3		
	nitrogen		HCl
sample	OA	TG	TG[a]
A	17	17	16
B	7	12	15

[a] Initial rate.

is almost zero. All these facts give a minimized induction period.

The dehydrochlorination rates for the samples are shown in Table II. The degradation rates for sample A in nitrogen are equal as mentioned above. However, for sample B there is a difference in the degradation rates for the two apparatus. This is due to the difference in the geometry of the apparatus which influences the flow characteristic. Sample B is also more sensitive to HCl which will catalyze the degradation. Poorer flow conditions in the TG increases the HCl concentration in the sample and therefore also the rate of dehydrochlorination.

The degradation curves for both samples degraded in an atmosphere containing HCl and in pure nitrogen are shown in Figure 3. The presence of HCl does not affect the initial degradation behavior in sample A. However, at high degrees of dehydrochlorination, above 1% deHCl, there is an increase in the degradation rate. For sample B, on the other hand, the dehydrochlorination rate is higher already from the start in the presence of HCl. However, the rate remains constant up to 0.7% deHCl, thereafter it increases. This autocatalytic behavior has

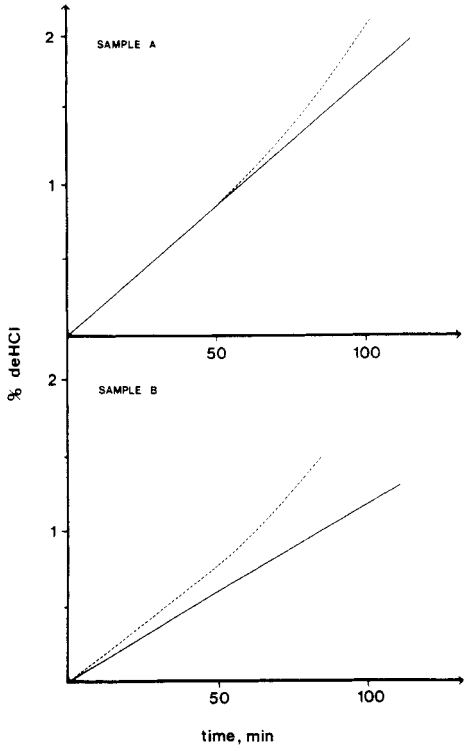


Figure 3. Degradation curves for sample A (above) and sample B (below). Degradation in nitrogen at 190 °C (—) and degradation in HCl at 190 °C (- - -).

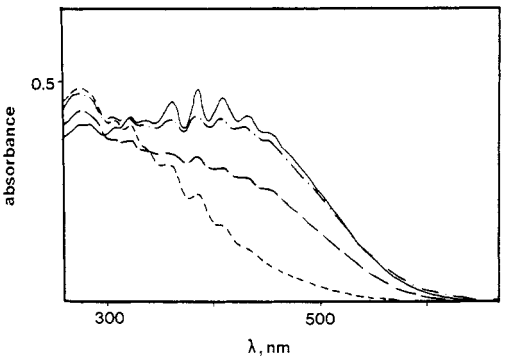


Figure 4. UV–visible spectra: sample A degraded in nitrogen (—) and in HCl (–·–); sample B degraded in nitrogen (- - -) and HCl (– –). All samples were degraded to 0.4% deHCl.

been observed in earlier investigations.[19]

Since the sample quantity in the TG is too small to provide material for the structural analysis, we had to do the remaining experiments in the OA. We calculated the degradation time in the OA, t_{OA}, to a certain degree of dehydrochlorination, d, in HCl atmosphere by

$$t_{OA} = d/r_{TG} + C \quad (4)$$

where r_{TG} is the dehydrochlorination rate in HCl atmosphere in the TG, and C the induction period in the OA. This equation is only approximate and the degrees of dehydrochlorination are not exact. In our earlier investigation[8] we found that sample B at the same degree of dehydrochlorination is less discolored than sample A. This decrease in discoloration is not due to secondary reactions but to the fact that the polyenes that are formed are shorter. The difference in polyene sequence length can be seen in the UV–visible spectra for samples A and B degraded in nitrogen to 0.4% deHCl, Figure 4. The longer the polyene sequences the more absorbance at long wavelengths. The spectra for samples A and B degraded in HCl, also Figure 4, show that sample A is not affected

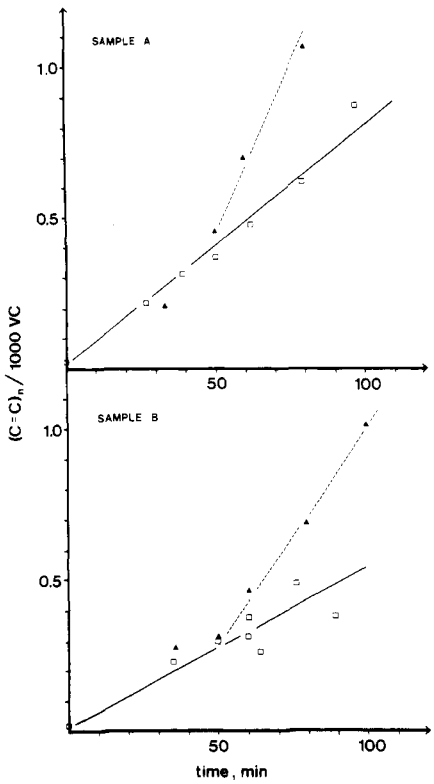


Figure 5. Number of polyene sequences versus degradation time for sample A (above) and sample B (below). Degradation in nitrogen (—) and degradation in HCl (- - -).

compared with the nitrogen degradation. At this degree of dehydrochlorination we did not notice any effect on the degradation rate in the TG experiments either. However, sample B degraded in HCl shows a marked change in the UV–visible spectrum, compared with the nitrogen degradation, i.e., the absorbance is much more pronounced at longer wavelengths. Accordingly the discoloration was more severe in the presence of HCl. As mentioned above we also observed a higher initial degradation rate for the sample degraded in HCl. This can be explained by the fact that longer sequences were formed. If each initiation point gives longer polyene sequences the dehydrochlorination rate must become higher.

We have also measured the number of polyene sequences with ozonolysis, where all double bonds are cleaved and the decrease in M_n is followed. The number of sequences can be calculated with eq 3. In Figure 5 we see the number of sequences versus degradation time for both A and B degraded in nitrogen and an atmosphere containing HCl. Under 50 min the number of sequences is the same for degradation in HCl and nitrogen but at longer degradation time the number of sequences for the samples degraded in HCl increases. These results are in accordance with the results obtained with the TG where the degradation rate increases in HCl atmosphere after a similar length of degradation time. The autocatalysis is therefore caused by increased initiation.

Discussion

When PVC is degraded in an atmosphere containing HCl there are two different effects of interest. (a) The increase in initiation of new sequences at high degrees of dehydrochlorination and (b) the increase in length of the polyene sequences as can be seen for sample B.

The increase in initiation was studied in an earlier investigation.[19] Since there is no increase at low degrees of dehydrochlorination, HCl itself does not seem to catalyze

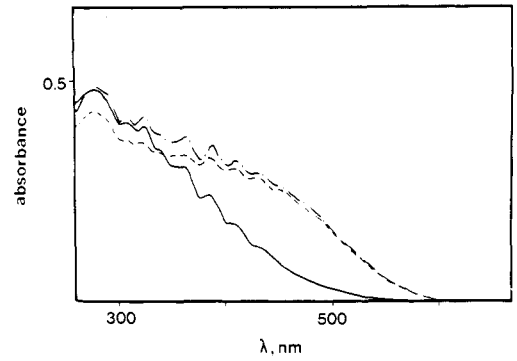
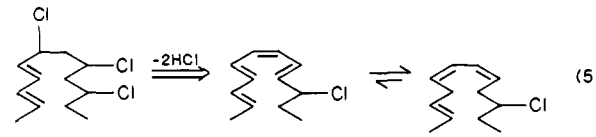


Figure 6. UV–visible spectra for sample B degraded in nitrogen (—), in HCl (- - -), and in nitrogen 58 min and thereafter in HCl for 2 min (-·-). All samples are degraded to 0.4% deHCl.

the initiation. At higher degrees of dehydrochlorination the formation rate of polyene sequences is increased. Therefore the catalysis of the initiation of polyene sequences is probably caused by cooperation between polyenes and HCl. This is in accordance with our earlier suggestion.

The influence of HCl on the length of the polyene sequence has been a matter of discussion in the literature; see, e.g., ref 20a. In our previous paper[8] we thoroughly discussed the subject and the result we then obtained made it possible to exclude some of the suggested mechanisms, such as the migration of double bonds along the chain, thus bringing sequences together,[21] and inhibition of secondary reactions, e.g., Diels–Alder reactions or intramolecular reactions.[11]

The most probable theory is that HCl influences either the elongation of the sequences or the stop reaction. Shapiro et al.[11] have suggested that the stop reaction is inhibited by HCl. An example of stop reaction can be cyclization at the growing end, assuming that the cyclization occurs when a trans double bond is formed after a cis:



(5)

As discussed in our previous paper[8] the equilibrium in reaction 5 should strongly favor the cyclic form. The cyclization or the retro reaction should further not be influenced by the polarity of the medium or by catalysts. It has, however, been proposed that acids may prevent the formation of cis double bonds or catalyze them into trans configurations.[22] Increased content of HCl would thus lead to longer sequences.

To examine whether the stop reaction or the elongation is affected by HCl we made degradation experiments with sample B in pure nitrogen to almost 0.4% deHCl (58 min) and then changed the atmosphere to HCl for 2 min. If we compare the UV–visible spectra for this degradation and the degradation in pure nitrogen, Figure 6, there is a marked increase in the absorbance at long wavelengths, i.e., an increased content of long polyenes. Compared with the total degradation time, the time in an HCl atmosphere is, however, very short, therefore the drastic change in polyene sequence length cannot be caused by the few new polyenes formed but by an elongation of all the polyenes in the sample. This is further demonstrated by the fact that there is no difference in polyene sequence length between this degradation and that of the same PVC degraded with HCl present from the beginning.

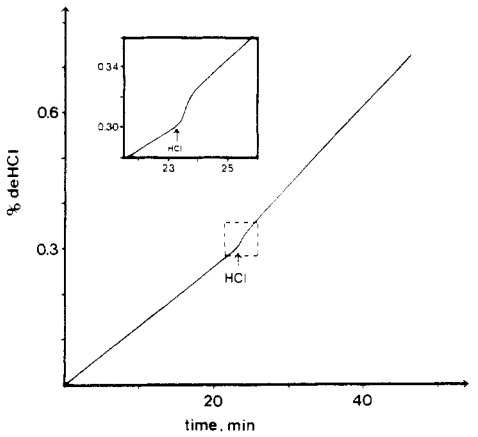
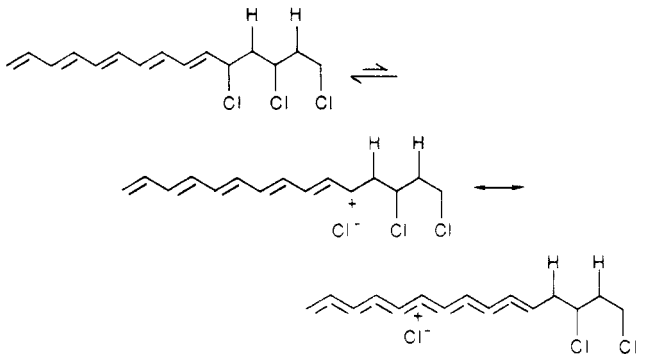


Figure 7. Degradation curve for sample B degraded in the TG. The degradation was performed in nitrogen up to 0.3% deHCl thereafter in HCl. The arrow indicates the change in atmosphere.

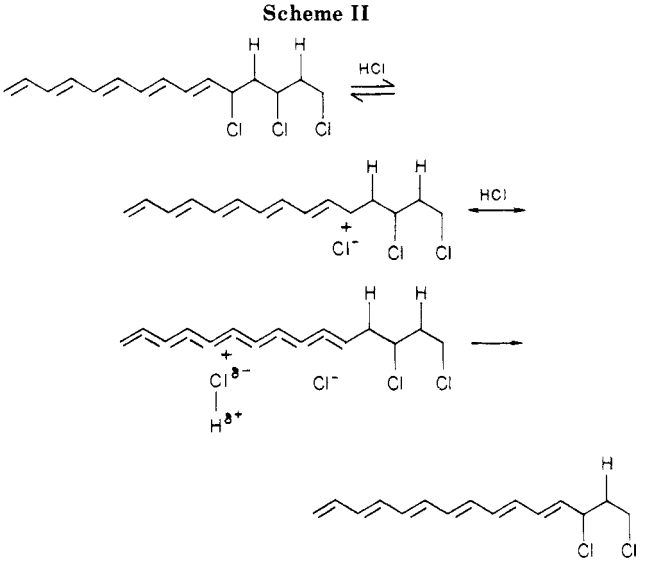
Scheme I



We also made the same experiment in the TG to follow the dehydrochlorination versus degradation time. As can be seen in Figure 7, there is a change in the degradation rate when HCl is added. Right after the addition a sudden increase in the dehydrochlorination can be discerned, see inset. In the figure we have compensated for the density difference between HCl and nitrogen. The sudden increase in dehydrochlorination and the change in the UV-visible spectrum are both a result of the lengthening of the polyene sequences. This strongly supports that the length of the polyene sequence is due to a kind of equilibrium reaction involving HCl rather than a stop reaction, e.g., (5), where a carbon–carbon bond has to be broken to achieve lengthening.

In the literature, several different mechanisms have been suggested for the polyene elongation. The suggestions include radical, ionic, and unimolecular (concerted) paths; see, e.g., ref 20b. We have proved that a decrease in the rate of dehydrochlorination causes the polyene sequences to become shorter and that the addition of HCl again produces longer polyene sequences. Obviously HCl has an important catalytic effect on the propagation step. We consider that the ion pair mechanism suggested by Starnes and Edelson[4,22,23] can account for these observations (Scheme I). In the ion pair mechanism the restricted length is due to that the conjugation energy for the polyenyl cations reaches a limiting value for long sequences. Molecular orbital calculations have shown that the positive charge has a strong tendency to concentrate in the center of the polyenyl cation.[24] This implies that the chloride counterion has less ability to migrate to the end of the sequence in order to abstract a proton from the methylene group. On the basis of this mechanism we suggest Scheme II to explain the HCl catalysis of the polyene propagation. There are two steps that could be influenced. The first

Scheme II



step is the formation of the ion pair. This is an equilibrium that should be shifted toward the ion pair in the presence of the polar HCl. The next step is the formation of the resonance structure. As already mentioned, the positive charge will concentrate into the center of the sequence and so will the negative chloride ion. In the presence of HCl the cation can be "stablized" by the partly negative chlorine in the HCl molecules. As HCl molecules occupy the center of the polyene, the chloride ion has less possibility of migrating to the center. It is therefore nearer the end of the sequence and more able to abstract a proton from the methylene group. The polyene sequences will therefore become longer until a new equilibrium length is reached.

Conclusions

HCl is an important element in the degradation of PVC. When PVC with improved thermal stability is degraded the concentration of HCl in the sample becomes lower. This affects the polyene sequence length so that the polyenes that are formed are shorter. When HCl is added during the degradation of this improved PVC the polyenes become longer again and the rate of dehydrochlorination increases. However, in the degradation of normal PVC, adding HCl does not seem to affect either the degradation rate or the length of the polyenes. This is because the amount of HCl in the sample is already sufficient to catalyze the lengthening of the polyenes. Our results enabled us to suggest a mechanism for the HCl catalysis of the propagation step in the degradation of PVC.

When a stabilized PVC is degraded there is no marked discoloration until the stabilizer is consumed; then it becomes black in a very short time. In this case the PVC is compact and all the HCl produced stays within the sample, thus leading to quick discoloration. To increase the time to "blackening" and achieve as little discoloration as possible during the induction period it is important to consider the effect of HCl when choosing or developing a new stabilizer system. The stabilizer must react effectively with HCl but also react with labile chlorine to lower the degradation rate and thus the discoloration, since this indirect effect of the HCl catalysis is of as much importance as the direct one.

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Registry No. PVC, 9002-86-2; HCl, 7647-01-0.

References and Notes

(1) Hjertberg, T.; Sörvik, E. M. *Polymer* **1983**, *24*, 673.
(2) Hjertberg, T.; Sörvik, E. M. *Polymer* **1983**, *24*, 685.
(3) Hjertberg, T.; Sörvik, E. M. In *Polymer Stabilization and Degradation*; Klemchuk, P. P., Ed.; ACS Symposium Series 280; American Chemical Society: Washington, DC, 1985; p 259.
(4) Starnes, W. H. In *Developments* in Polymer Degradation-3; Grassie, N., Ed.; Applied Science: London, 1981; p 135.
(5) Starnes, W. H.; Plitz, I. M.; Hische, D. C.; Freed, D. J.; Scilling, F. C.; Schilling, M. L. *Macromolecules* **1978**, *11*, 373.
(6) Starnes, W. H.; Haddon, R. C.; Hische, D. C.; Plitz, I. M.; Schosser, C. L.; Schilling, F. C.; Freed, D. J. *Polym. Prepr.* **1980**, *21* (2), 176.
(7) Ivan, B.; Kennedy, J. P.; Kelen, T.; Tudos, F.; Nagy, T. T.; Turcsanyi, B. J. *Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2177.
(8) Hjertberg, T.; Martinsson, E.; Sörvik, E. *Macromolecules*, in press.
(9) Mitani, K.; Ogata, T.; Nakatsukasa, M.; Eda, Y. *J. Macromol. Sci. Chem.* **1977**, *A11*, 2265.
(10) Suzuki, T. *Pure Appl. Chem.* **1977**, *49*, 539.
(11) Shapiro, J. S.; Starnes, W. H.; Plitz, I. M.; Hische, D. C. *Macromolecules* **1986**, *19*, 230.
(12) Toa Gosei Chemical Industry Ltd., Patent application, JA-089152, 1978.
(13) Toa Gosei Chemical Industry Ltd., Patent application, JA-089154, 1978.
(14) Abbås, K. B.; Sörvik, E. M. *J. Appl. Polym. Sci.* **1973**, *17*, 3567.
(15) Abbås, K. B.; Sörvik, E. M. *J. Appl. Polym. Sci.* **1975**, *19*, 2991.
(16) Drott, E. E.; Mendelsson, R. A. *J. Polym. Sci. Polym. Phys. Ed.* **1970**, *8*, 1361; **1970**, *8*, 1373.
(17) Michel, A.; Schmidt, G.; Guyot, A. *Polym. Prepr.* **1973**, *14*, 665.
(18) Kelen, T. *J. Macromol. Sci. Chem.* **1978**, *A12*, 349.
(19) Hjertberg, T.; Sörvik, E. M. *J. Appl. Polym. Sci.* **1978**, *22*, 2415.
(20) Hjertberg, T.; Sörvik, E. M. In *Degradation and Stabilization of PVC*; Owen, E. D., Ed., Elsevier Applied Science: London, 1984; (a) p 53, (b) p 41.
(21) Owen, E. D.; Pasha, I.; Moayyedi, F. *J. Appl. Polym. Sci.* **1980**, *25*, 2331.
(22) Starnes, W. H.; Edelson, D. *Macromolecules* **1979**, *12*, 797.
(23) Starnes, W. H.; Edelson, D. *Am. Chem. Soc., Div. Org. Coat. Plast. Chem. Pap. Meet.* **1976**, *41*, 505.
(24) Haddon, R. C.; Starnes, W. H. *ACS Adv. Chem. Ser.* **1978**, *169*, 333.

Homopolygalacturonan Nitroxyl Amides: Hydration-Induced Motion

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ABSTRACT: In order to understand the relationship between the degree of polymer hydration, axis of rotation, and rotational frequency as well as rotational anisotropy, we measured the EPR spectra of variably hydrated nitroxyl amide spin-labeled plant homopolygalacturonan (PGA) solids from 77 to 342 K. Detailed spectroscopic simulations using stochastic Liouville theory gave the best fit for experimental spectra assuming a moderate jump model with a rotational anisotropy of 3. The axis of rotation was the magnetic y axis of the nitroxyl amide which corresponds to rotational motion about the polymer's main chain. Internal motions of the dry polymer's nitroxyl ring NH–C bond were found to have two activation energies (0.4 and 3.5 kcal/mol) in the experimental temperature range (77–342 K), indicating a temperature-dependent perturbation of the acid sugar polymer's intermolecular structure. EPR studies of solid matrices with various levels of hydration showed two motional domains corresponding to spin labels with different levels of rotational hindrance. We propose that the "slow" component was due to that fraction of the spin population in highly aggregated helical domains while the "fast" component resulted from isolated blocks of main chain motion due to localized disruption of the ordered matrix. The spin population representing the fast motional domain became the most dominant component of the EPR spectrum upon increasing the temperature and degree of hydration. However, further spectral analysis revealed that the fast component's motion was incompletely averaged and, therefore, was not wholly isotropic.

Introduction

Electron paramagnetic resonance (EPR) has been shown to be an excellent technique to characterize the microstructural and dynamic properties[1-3] of various species. Nitroxyl spin labels have been widely used as probes to obtain information about the nature of localized molecular properties such as conformation, flexibility, and solute–solvent interactions in diverse systems such as poly(phenylacetylene),[4] poly(vinyl alcohol) gels,[5] liquid crystals,[6] vesicles,[7] nucleic acids,[8] lipids, and proteins.[9,10] It has been only within the last several years that a significant amount of work on spin-labeled carbohydrates has appeared in the literature,[11] even less research has been performed on polysaccharides as they exist in their native state. From our laboratory, evidence has been recently presented which indicates that the nitroxyl amine, utilized in this work,[12] covalently attaches through an amide bond to sugar acid polymers in a spatially sequential fashion.

The cell walls[13] of higher plants are roughly analogous to the skeleton of animals. These exceedingly complex, mostly polysaccharide, matrices are biologically important because they modulate cell structure and morphology and act as a primary size exclusion barrier to small molecules as well as pathogenic organisms. One of the most important structural polysaccharides[14,15] of higher plant primary cell wall and middle lamellar complexes are the polygalacturonan-containing macromolecules. The most characteristic physical property of this family of polymers is their ability to form rigid gels[16] and extended arrays[17-19] under aqueous conditions. However, little is understood about the higher order structure[20] of these macromolecules in their natural state (e.g., as a solid). Under such con-

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