1810 *Macromolecules* 1985, *18*, 1810–1818

Photothermal Dehydrochlorination of Poly(vinyl chloride)

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Received September 14, 1984

ABSTRACT: The photothermal dehydrochlorination of PVC has been investigated by the new spectroscopic methods absorption derivative spectroscopy and excitation–emission fluorescence matrix spectroscopy. The UV irradiation accelerates a rapid evolution of HCl from thermally treated PVC samples; the evolution was measured by sensitive conductometric methods. It has been found that the quantum yield of HCl evolution increases with increasing temperature. It has been suggested that in the initiation step carbonyl and/or hydroperoxide groups play a more important role than the residual double bond present and the double bond formed during photothermal dehydrochlorination of PVC. A mechanism involving electronic-to-vibrational energy transfer has been proposed in order to explain accelerated photothermal dehydrochlorination of PVC.

Introduction

Studies of poly(vinyl chloride) (PVC) dehydrochlorination and oxidation upon exposure to light[1-18] and heat (150–220 °C)[19-38] have previously been reported. In spite of great effort, the reasons for the high instability of PVC are not explained yet, and the interpretations are not adequately experimentally proved. These problems have been the subject of several reviews[35,39-44] that attempt to consider all possible factors which may enhance instability of PVC under light and heat. During dehydrochlorination and oxidation accompanied by chain scission and cross-linking, the mechanical properties of PVC solids, such as brittleness, elongation, and tensile strength, change rapidly.[45-47]

During the last decade there has been growing interest in the possibility of applying polymers to the use of solar energy.[48] In such applications polymeric materials are exposed simultaneously to light and heat. Several new problems arise in much more complicated environmental degradation conditions. Specifically, an initiation mechanism of photodegradation should be activated by higher temperatures. This problem was only partially investigated by others[4,15,17] and was mainly limited to the experiments performed in nitrogen or a vacuum.

We were interested in the study of the initiation mechanism of photothermal dehydrochlorination of PVC for which we have used derivative and excitation–emission matrix fluorescence spectroscopy (EEMFS). The results concerned with this problem and some new suggestions not published previously are presented in this paper.

Experimental Section

Suspension-polymerized PVC (Pevikon S-658) was obtained from Kema-Nord AB (Sweden) in the form of white powder: (manufacturer's data) Fikentscher *K* value 66; $\bar{M}_n$ = 56 000; $\bar{M}_w$ = 145 000, i.e., polydispersity factor 2.59.

The total number of double bonds has been measured by bromination in 1,2-dichloroethane in the presence of mercuric acetate as catalyst in the dark.[49]

PVC films (30–50 μm) were cast from 1,2-dichloroethane (UVASOL, Merck) and used for the measurements of HCl evolution kinetics and for the study of EEMFS spectra.

PVC solutions (6×10^{-1} M) in tetrahydrofuran (THF) (UVASOL, Merck) were used for the measurements of absorption and derivative spectra. Samples were dissolved in THF directly before spectrophotometric measurements in the dark in order to avoid the photooxidation of THF to α-(hydroperoxy)tetrahydrofuran, which can be responsible for sensitizing photodegradation of PVC and also for the reaction with polyenes (bleaching reactions).[9,14,50-55]

Irradiations were performed at different temperatures in the arrangement shown in Figure 1. The UV radiation from a high-pressure Hg lamp type HPM-15 (1000 W) supplied by Philips (Holland)[56] (1) passed through a quartz water-cooling filter (2). For separation of the required wavelength with full width at half-maximum (10 ± 2 nm) a combination of variable band-pass and interference filters was used with peak transmission 40–60% (3), delivered by Melles Griot, Holland. PVC film samples (5) were placed in the flow in–out flat quartz cell (4). The fraction of incident light absorbed by the initial and irradiated films was measured by radiometer/photometer system Model 550 (8) with detector Model 550-2 multiprobe (7) and monochromator Model 555-61 (6) delivered by EG&G Electro Optics, USA. All irradiations of PVC samples were performed in a flow of air, which was used in order to perform oxidative reactions and to remove HCl evolved from irradiated and thermally heated samples. Air from a high-pressure cylinder (9) passed through a water trap filled with Ascarite (10) and through a flow meter (11) (300 mL/min) and was then heated to the required temperature in the spiral heating oven (12) with an accuracy of ±0.1 °C controlled by the thermoregulator-type Pentronic (13) delivered by Gunnebo Bruk, Sweden. The air at constant flow and required temperature met the PVC sample (5) in a flat quartz cell (4) that was thermostated. The HCl evolved during the experiments was removed by the air flow from the quartz cell and passed through the water-cooled cooler (14). It entered into the conductometric cell (15) where it was completely absorbed in 30 mL of doubly distilled water. The electrical conductivity of the solution was measured by an elctrode cell (Type EA 608-01, Methrom Herisau, Switzerland) with the constant $C = 0.0785\ \mathrm{cm}^{-1}$ connected to a conductometer Type E518 (16) delivered by Methron Herisau, Switzerland, with automatic correction for temperature variations. HCl concentrations of about 10^{-7} M could be measured, corresponding to evolution of about 10^{-4}% of HCl when a 0.3-g sample of PVC was used.

UV/vis absorption and derivative spectra (in THF solutions at concentrations 6×10^{-1} M of PVC) were recorded by Perkin-Elmer 575 UV/vis and Gilford System 2600 spectrometers, respectively.

Excitation–emission matrix fluorescence spectra (EEMFS) were recorded from PVC films by a Perkin-Elmer luminescence Type LS-5 spectrophotometer with a Data Station computer system Type 3600 and a Type R100 recorder.

The quantum yield of the photothermal dehydrochlorination was obtained from the slope of the curves of the amount of HCl evolved vs. irradiation time at a given temperature, determined by titration using 0.01 N aqueous NaOH vs. the number of photons absorbed[56] after subtracting the amount of HCl that is evolved in thermal dehydrochlorination without irradiation.

Results and Discussion

The poly(vinyl chloride) (PVC) contains only C–C, C–H, and C–Cl bonds and is not, therefore, expected to absorb light of wavelength longer than 190–220 nm. The fact that free radicals are formed after irradiation with UV light of longer wavelengths indicates that some kinds of chromophores must be present in PVC samples.[41,43,57] The light and heat instability of PVC must be caused by structural abnormalities that are present to varying extents in different types of commercially available PVC samples, such as random unsaturation (allylic chlorines),[38,58-61] chain end

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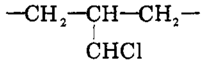
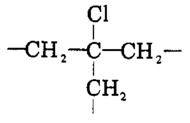
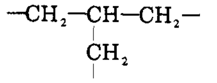
Table I
Structural Defects in PVC[61]

	possible transformation products	
unsaturated end groups	long branches	abnormal internal structures
$-CH_2-CHCl-CCl=CH_2$ $-CH_2-CHCl-CH=CH_2$	 $-CH_2-\underset{CHCl}{\underset{\vert}{CH}}-CH_2-$	$-CH_2-CCl=CH-CH_2-$ $-CH_2-CH=CH-CH_2-$
$-CH_2-CHCl-CH_2-CCl=CH_2$	 $-CH_2-\overset{Cl}{\overset{\vert}{\underset{\underset{\vert}{CH_2}}{\underset{\vert}{C}}}}-CH_2-$	$-CH_2-CHCl-CH_2-CCl=CH-CHCl-CH_2-$
$-CH_2-CHCl-CH_2-CH=CH_2$	 $-CH_2-\underset{\underset{\vert}{CH_2}}{\underset{\vert}{CH}}-CH_2-$	

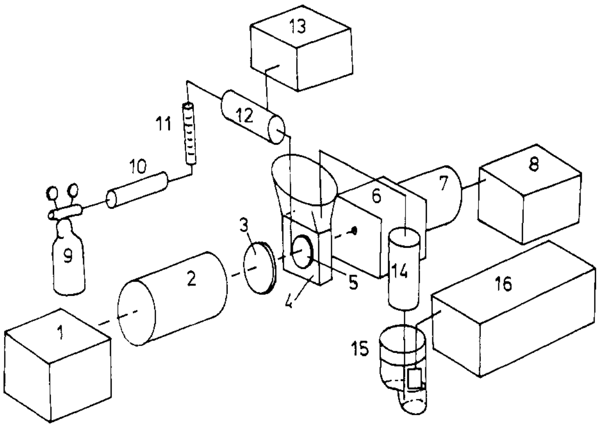


Figure 1. Schematic diagram of apparatus used for the study of photodehydrochlorination, thermal dehydrochlorination and photothermal dehydrochlorination of solid PVC samples. Detailed description of the elements are given in the Experimental Section.

groups,[27,29,36,58,61] branch points (tertiary-bonded chlorine atoms),[27,29,37,50,61-63] head-to-head units,[29,58,61,64,65] and oxidized structure.[29,61,66-68] Caraculacu[61] presents the number of defects per 1000 monomer units in commercial PVC samples as follows: 4–6 chloromethyl branches, 0.4–2.4 chloroethyl branches, 0.4–1.6 butyl branches (uncertain value), 0.18–2.4 long branches (uncertain value), 6–7 head-to-head structures (uncertain value), 1.4–3 total double bonds, and 0.08–0.27 internal double bonds. Labile chlorine atoms have been estimated at 0.6–2.5 per 1000 monomer units of which 0.5–2.5 are allylic chlorine or ketochloroallylic chlorine and 0.16–1 are chlorine at tertiary carbon (uncertain value).

The possible structures of these defects are given in Table I. In addition to these structural defects several oxygen-containing groups such as ketonic carbonyl (CO), aldehyde (CHO), hydroperoxide (OOH), and ether links (-O-) can be formed during polymerization and storage of PVC in the presence of air. PVC samples can also contain traces of catalysts or products of their decomposition.

The PVC sample used for the experiments gives a weak absorption spectrum within 250–500 nm without distinguished peaks (Figure 2). Application of derivative spectroscopy shows several absorption peaks in the range 250–300 nm (260, 262, 267, 272, 282, and 289 nm) of different intensity (289 nm has the strongest intensity) (Figure 2). The original sample does not exhibit peaks that could be attributed to polyene structures with $n > 4$ (where n is the number of double bonds present in a given polyene sequence). The EEMFS spectra show that the PVC sample exhibits weak fluorescence emission (Figure 3) when excited in the range 260–310 nm. The emission can be assumed to be due to a small amount of different types of carbonyl groups present in the starting material. These carbonyl impurities are impossible to remove by extraction with common solvents, indicating that they are permanently attached to the PVC molecules. They are probably residues of catalysts used for suspension polymerization (the producer did not supply us with information on the type of catalyst used) or are the results of a slow environmental oxidation of commercial products.

The double bond content (analyzed by bromine addition) in the starting PVC samples has been found to be 3.15 per 1000 mers. It is quite probable that the derivative absorption band at 289 nm (Figure 2) can be attributed to the presence of these double bonds rather than to carbonyl groups that have absorption in the range 260–280 nm.

It is generally accepted that photodehydrochlorination,[1-18] thermal dehydrochlorination,[19-38] and radiative[69-72] dehydrochlorination occurs with discoloration of the polymer due to polyene formation. Long sequences of polyenes are formed, especially in a vacuum,[69,70] whereas under oxygen, formation of long polyene sequences is hindered by oxidative attacks on the conjugated double bonds. Oxygen in general accelerates dehydrochlorination of PVC especially in thermal degradation.[32,44,73-75]

One of the problems still unsolved in the photodegradation of PVC concerns the initiation step involving absorption of light by PVC. The absorbing chromophores responsible for the initiating step can be divided into two main groups:

(i) Unsaturated structures such as dienes (ϵ = 42 000 L mol^{-1} cm^{-1})[76] and trienes (ϵ = 210 000 L mol^{-1} cm^{-1})[76] that are present in the original sample and that accumulate during UV irradiation.[43] Polyenes in the excited singlet state have the following energies: trienes (107 kcal mol^{-1}), tetraenes (84 kcal mol^{-1}), and pentaenes (84 kcal mol^{-1}).[77] The bonds that are primarily cleaved in the photolysis of PVC are the labile allylic C–Cl bonds whose dissociation energy (78 kcal mol^{-1}) would be increasingly lowered as the polyene length is growing.[5,16] Irradiation of a PVC sample that contains a polyene sequence with n = 14 conjugated bonds with visible light (at 514.5 nm) gives similar ϕ_{HCl} as during irradiation of the sample with 250–400 nm. These results strongly suggest that the dissociation energy of the C–Cl bond next to the end of a polyene with 14 conjugated double bonds can be as low as 55 kcal mol^{-1}, or even less.[5,16]

(ii) Oxygen-containing groups (CO, CHO, and OOH) show much lower molar absorptivities than polyenes.[78] Carbonyl groups in the excited triplet states have energies in the range 65–90 kcal mol^{-1}.[79] Excited carbonyl groups

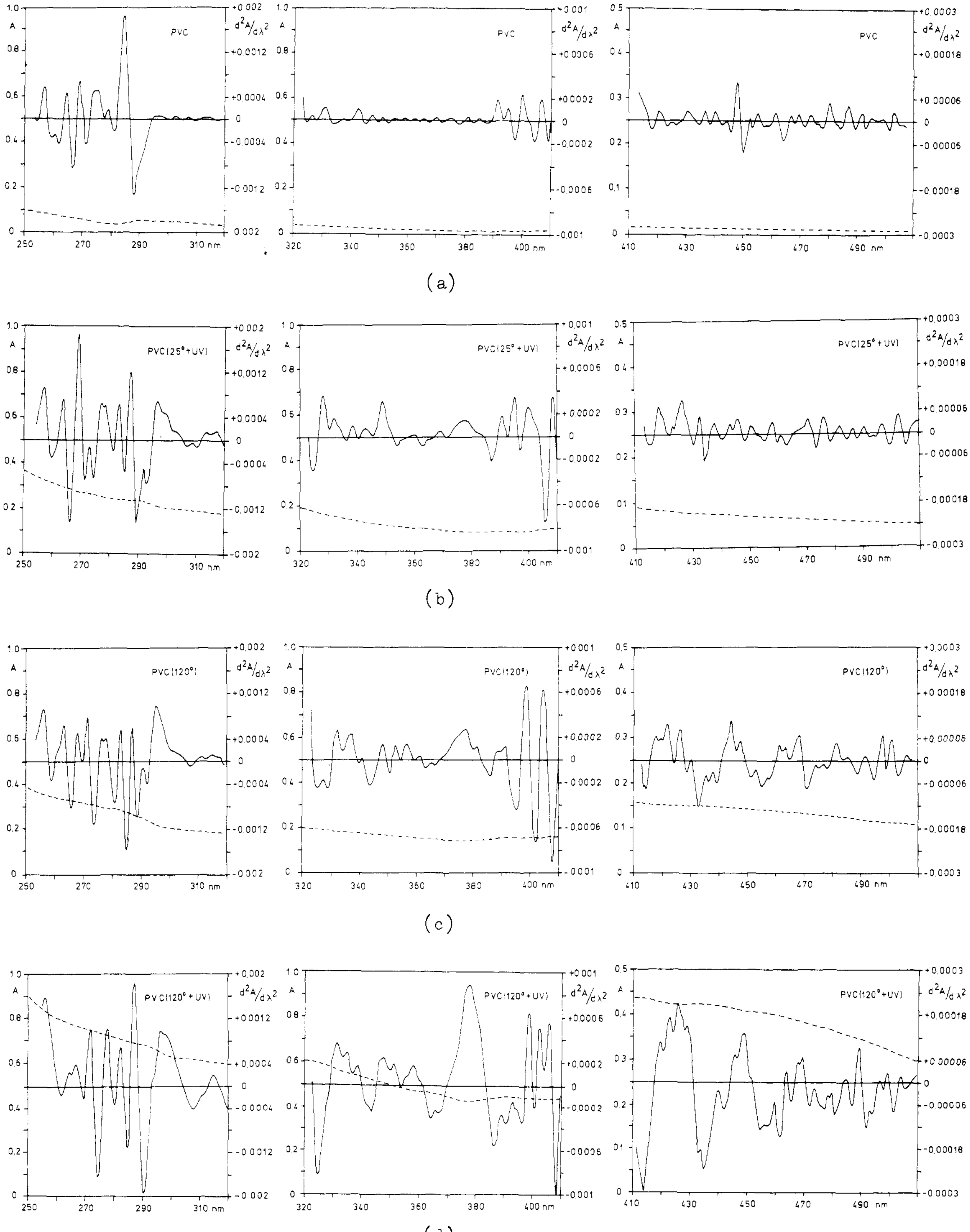


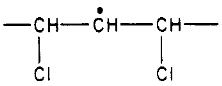
Figure 2. UV/vis absorption (broken line) and UV/vis absorption derivative (continous line) spectra of PVC in THF (6×10^{-1} M): (a) pure sample; (b) PVC sample UV irradiated at 25 °C (3 h); (c) PVC sample heated at 120 °C (3 h); (d) PVC sample simultaneously UV irradiated and heated at 120 °C (3 h).

undergo three common bifunctional reactions: hydrogen abstraction, electron transfer, and electronic energy transfer. Each of these processes can occur by inter- and intramolecular reactions, which depend on the conformational equilibrium of macromolecules. All of these three processes occur from both excited singlets and triplets.

The latter are more important with regard to competition with conformational motion of macromolecules. Decker and Balandier[16] suggest that carbonyl and hydroperoxides are not expected to take an important part in the initiation step. In contrast, it has been published that the rate of photooxidation of unstabilized PVC is markedly dependent on the severity of the processing operation[12,44] during which carbonyl and hydroperoxide groups are formed. It has also been suggested that α-chloro ketone structures[80] may play a more important role than allylic C–Cl in the initiation of PVC photodehydrochlorination.

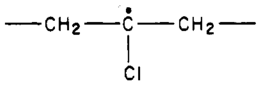
Both polyene chromophores and oxygen-containing groups may participate in energy-transfer processes.[5]

A new mechanism of initiation of polymer photodegradation has been previously proposed by Rabek.[81] In this mechanism reactions resulting from electronic–vibrational coupling lead to the excitation of specific molecular vibrations. Such coupling is strongest with high-energy stretching vibrations, and these vibrations are known to be the preferred energy acceptors in radiationless relaxation processes.[82-84] The abundance of photochemical hydrogen abstraction from tertiary carbon and even from methylene groups (CH_2) can be explained by preferential electronic energy transfer to stretching vibrations involving hydrogen, which are of relatively high frequency. The quantum yield of this reaction should be high when the rate of reaction of the vibrationally excited molecule exceeds the rate of vibrational relaxation. In PVC hydrogen atoms in methylene groups are involved in the high-frequency molecular vibrations. When vibrations can be assigned to stretching modes of bonds and for bonds of similar vibrational frequencies, the lower the heat of formation of the bond or the more anharmonic the vibration, the more reactive the bond is.[82] In the radiationless relaxation processes (in which electronic energy is converted into vibrational energy) the best energy-accepting vibrations are the more anharmonic vibrations that approach most closely the electronic energies. These are usually anharmonic stretching vibrations with high-vibrational energies that involve stretching of the weaker bonds of carbon with hydrogen, the lightest atom. In the electronic–vibrational coupling mechanism electronic energy flows preferentially to stretching vibrations involving hydrogen atoms whenever a radiationless relaxation takes place. This mechanism can be responsible for the formation of the different types of polymer alkyl radicals such as I and II in the photoinduced initiation step of photodehydrochlorination of PVC.



$$-\underset{Cl}{CH}-\dot{C}H-\underset{Cl}{CH}-$$

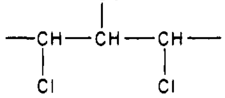
I



$$-CH_2-\underset{Cl}{\dot{C}}-CH_2-$$

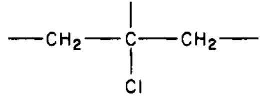
II

Polymer alkyl radicals are very reactive with molecular oxygen and produce polymer peroxy radicals III and IV whose presence has been proved in PVC by ESR spectroscopy.[10,85,86]



$$-\underset{Cl}{CH}-\overset{OO\cdot}{CH}-\underset{Cl}{CH}-$$

III

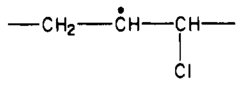


$$-CH_2-\underset{Cl}{\overset{OO\cdot}{C}}-CH_2-$$

IV

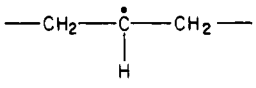
In contrast, the carbon–chlorine bond scission also yields polymer alkyl radicals of types V and VI and chlorine radical (Cl·).

Formation of radicals V and VI has been confirmed by ESR spectroscopy.[87,88] Polymer alkyl radicals V and VI react with oxygen to produce polymer peroxy radicals of types VII and VIII. The propagation reactions by peroxy radicals should generate mostly radical IV, since a tertiary C–H bond is about 25 times more reactive than a secondary C–H bond toward alkylperoxy radicals at 25 °C,[6,89] so that the main oxidation products of PVC are assumed to result principally from the reaction of the α-chloroalkyl peroxy radical (IV).



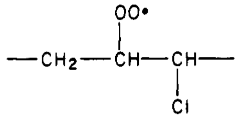
$$-CH_2-\dot{C}H-\underset{Cl}{CH}-$$

V



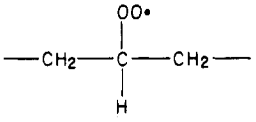
$$-CH_2-\underset{H}{\dot{C}}-CH_2-$$

VI



$$-CH_2-\overset{OO\cdot}{CH}-\underset{Cl}{CH}-$$

VII



$$-CH_2-\underset{H}{\overset{OO\cdot}{C}}-CH_2-$$

VIII

In consequence of the formation of polymer peroxy radicals, the carbonyl (CO) and hydroperoxide (HOO) groups are produced. The presence and kinetics of formation of these groups (CO at 1720 cm^{-1} and HOO at 3450 cm^{-1}) can be monitored easily by IR spectroscopy.[7,10,12,13,32,73]

Owen and Reid[90,91] have studied fluorescence emission and excitation spectra of dilute THF solutions of thermally or photochemically degraded PVC. These spectra are difficult to interpret. Fluorescence techniques make it possible to study an early initiation step when any change can be detected by absorption spectroscopy or HCl evolution. We[90,91] presented only spectra at excitation wavelengths 250 and 340 nm. These emission spectra were attributed to the presence of polyene structures (n = 4–6) and α- and β-unsaturated ketones.

The EEMFS spectra (Figure 3) obtained in our experiments show the formation of different chromophoric groups during UV irradiation (Figure 3b), thermal treatment (at 120 °C) (Figure 3c), and both effects employed simultaneously (Figure 3d). In the case of UV irradiation (at 25 °C) chromophoric groups with strong emission in the range 260–500 nm are formed. Some of these chromophoric groups are thermally decomposed at 120 °C and do not exist or exist in low concentration. Derivative absorption spectra (Figure 2) show that during photothermal dehydrochlorination of PVC (125 °C + UV) (Figure 2d) polyene structures are formed (309, 325, 340, 365, 387, 391, 397, 401, 415, 435, 455, 462, 467, 477, 481, 492, and 502 nm). Many of these absorption bands are also formed during thermal degradation of PVC (120 °C) (Figure 2c) but at much lower concentrations. PVC samples irradiated only with UV radiation at room temperature (25 °C + UV) (Figure 2b) do not show such evident formation of polyenes with longer n sequences. It is easily seen that application of the absorption derivative spectroscopy has strong advantages over the absorption transmittance spectroscopy. A very accurate position of every formed absorption band can be determined. Complete analysis of these bands at the moment is impossible and requires study with model compounds, which will be subject of our forthcoming research.

Successive dehydrochlorination reactions adjacent to the free radical may generate long-chain polyenyl-free radicals at constant concentration. ESR studies of PVC samples γ-irradiated in a vacuum[69,92] or thermally dehydrochlorinated[21,22,93] give a single line ESR spectrum that has been attributed to the formation of polyenyl radicals. The polyenyl radical is very stable under vacuum and even at

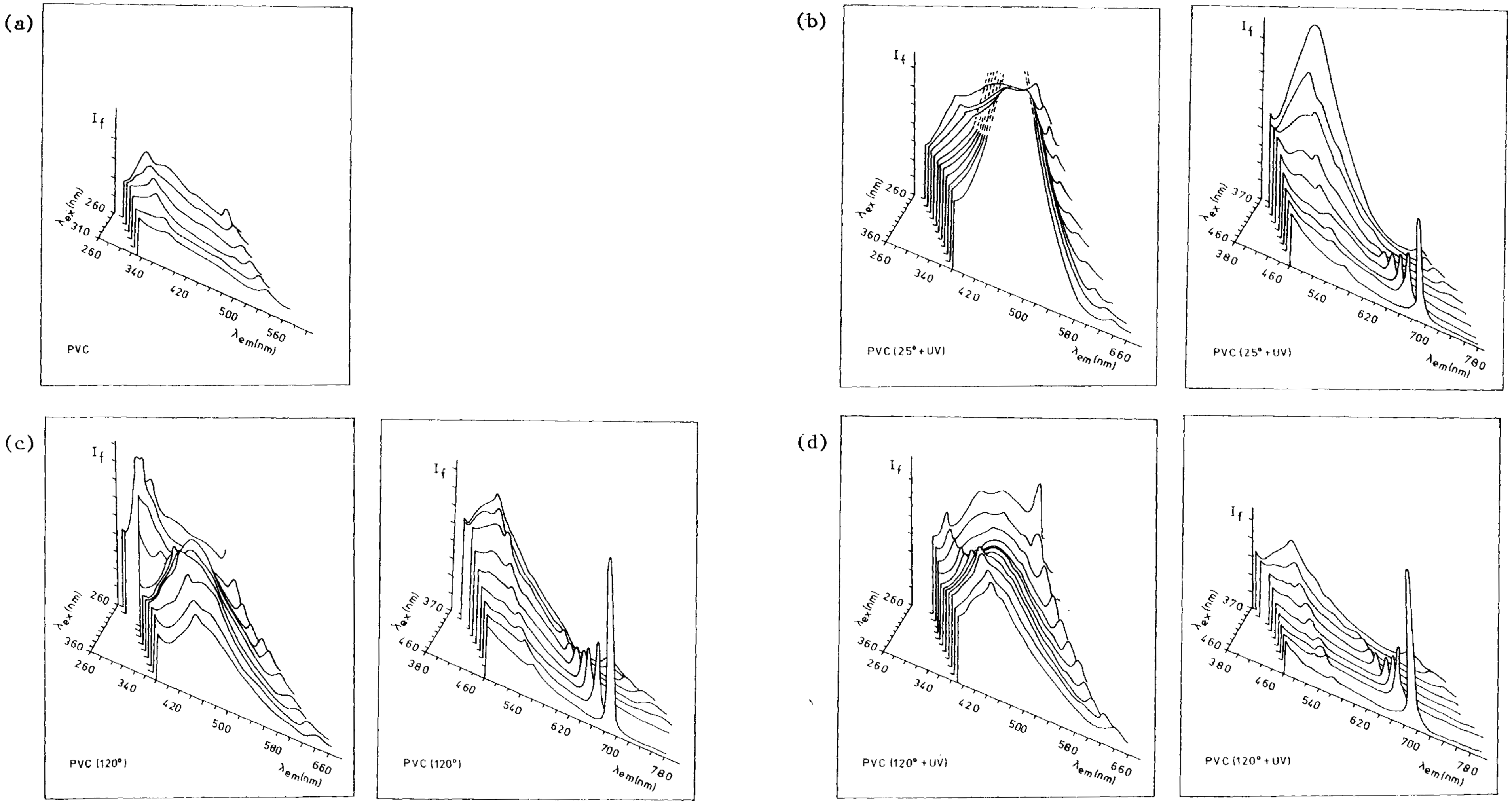


Figure 3. Excitation–emission fluorescence matrix spectra (EEFMS) of solid PVC films expressed as fluorescence intensity (I_f) at different emission wavelength (λ_{em}) during excitation with different wavelengths (λ_{ex}): (a) pure PVC sample, (b) PVC sample UV irradiated at 25 °C (3 h); (c) PVC sample heated at 120 °C (3 h); (d) PVC sample simultaneously UV irradiated and heated at 120 °C (3 h).

high temperature (120 °C). These results show the delocalization of the electron in polyenyl-free radicals that may exist as solitons, analogous to that found in polyacetylenes.[94] In the presence of oxygen, polyenyl radicals are scavenged and the radical concentration decays.

The dehydrochlorination is an equilibrium reaction that may be controlled by the rate of diffusion of HCl outside the sample. This rate is in turn dependent on the surface area of the sample under degradation and on the internal mobility of chains inside the sample, which increases with increasing temperature and decreases with progressive cross-linking reactions. Talamini and Pezzin[95] have observed that HCl evolution during the thermal degradation of PVC is an accelerating process. The higher rate of dehydrochlorination may be due to the decomposition products of peroxides in thermooxidative degradation.[96,97]

Two major chain processes occur simultaneously during thermal degradation of PVC: (i) zip dehydrochlorination that proceeds efficiently, regardless of the presence or absence of oxygen, and yields polyene structures and HCl and (ii) the oxidative chain processes that lead to the formation of hydroperoxide, dialkyl peroxide, and carbonyl groups, together with cross-linking and chain scission reactions.

Increasing the temperature may favor the HCl diffusion out of the sample and decrease the autocatalytic effects.[89] The initiation, propagation, and termination steps in the thermal degradation of PVC at higher temperatures (190–220 °C) are catalyzed by HCl.[31,34] The low initiation efficiency partly results from the restricted mobility of the free radical fragments in a solid polymer irradiated at temperatures below T_g (87 °C), which favors radical recombination. In contrast, when PVC was photolyzed in solution, where cage reactions are less likely to occur, the quantum yield of initiating radicals was found to be much larger and dehydrochlorination to proceed 10 times more efficiently.[14]

The zip dehydrochlorination proceeds basically in a cage reaction, which explains why long polyenes are mostly found in PVC photolyzed in the solid state. In solution, where the chlorine radical (Cl·) can more easily diffuse out of the cage, growth of polyene sequences is less favored and discoloration much less pronounced.[14]

The presence of gaseous HCl accelerates the photooxidation reaction of PVC.[89] Two interpretations have been proposed. In the first, HCl acts as a chain-transfer agent, reacting with a radical such as ROO· to give a very reactive chlorine radical (Cl·).[98] In the second, HCl solubilizes metallic impurities, giving metallic salts whose catalytic effect on oxidation reactions is well-known.[99]

Using the HCl evolution for the calculation of the kinetics of dehydrochlorination is not accurate because it has been shown that the polymer partially retains HCl[97] and that HCl can react with polyenes via photochemical addition.[18,100–103] Study of the kinetics of HCl evolution during UV, thermal, and photothermal degradation (Figure 4) shows that the amounts of produced HCl differ significantly depending on the treatment of the PVC samples. During the heating of PVC samples up to 100 °C the amount of HCl formed was very low. It increases rapidly at 120 °C. When PVC samples were UV-irradiated at room temperature (25 °C + UV) the amount of HCl produced was higher than in the case of thermal dehydrochlorination at 100 °C. Parallel UV irradiation and heating at 50, 80, 100, and 120 °C of PVC samples show the extremely high increase of HCl produced in photothermal dehydrochlorination reactions. UV and thermal dehydrochlorinations of PVC samples show the existence of an induction period, which has been shown separately in Figure 5.

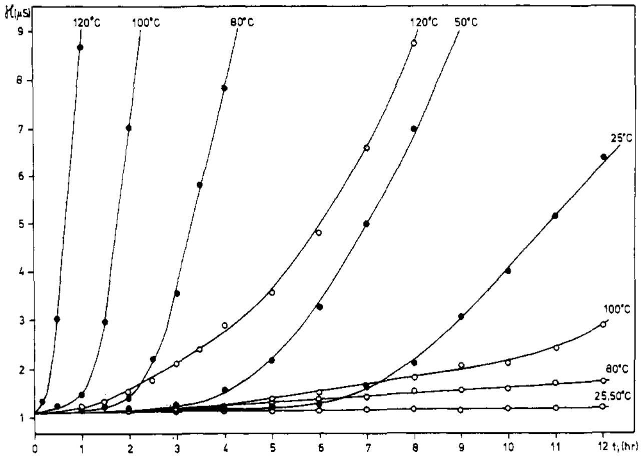


Figure 4. Kinetics of HCl evolution from PVC solid samples expressed as conductivity units (μS) at different irradiation times (t_i) (h): (○) heated at different temperatures, 25, 50, 80, 100, and 120 °C; (•) simultaneously UV irradiated and heated at 25, 50, 80, 100, and 120 °C.

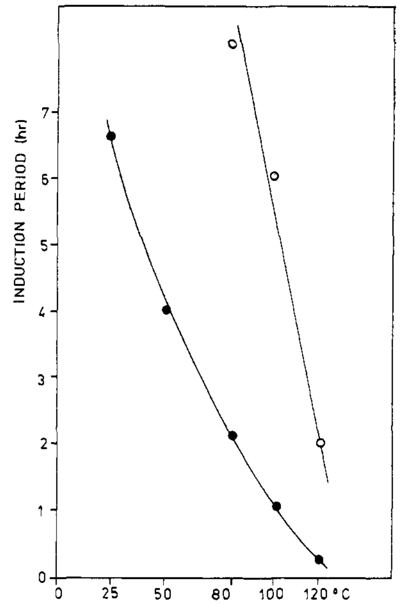


Figure 5. Induction period for HCl evolution from PVC solid film samples measured for the same conductivity, ϰ = 1.5 μS: (○) heated at different temperatures, 80, 100, and 120 °C; (•) simultaneously UV irradiated and heated at 25, 50, 80, 100, and 120 °C.

The analysis of double bond concentration formed during UV irradiation after 3 h shows that the number of these bonds increases from 3.15 to 4.6 per 1000 monomer units; a similar result has been obtained after 3-h heating of PVC samples at 100 °C, where the amount of double bonds increased from 3.15 to 4.6 per 1000 monomer units. Analysis of absorption derivative spectra (Figure 2b,2c) supports these results. The EEMFS spectra (Figure 3b) show that during this time of irradiation (3 h) strong oxidation of PVC samples occurs. The main process during the initiation step is the oxidation of free radicals formed rather than the formation of polyene structures. In our opinion the PVC sample that accumulates enough concentration of carbonyl and hydroperoxide groups is more sensitive to photo- and/or thermal dehydrochlorination. These groups must play an important role in the mechanism of initiation, rather than the unsaturated bonds as

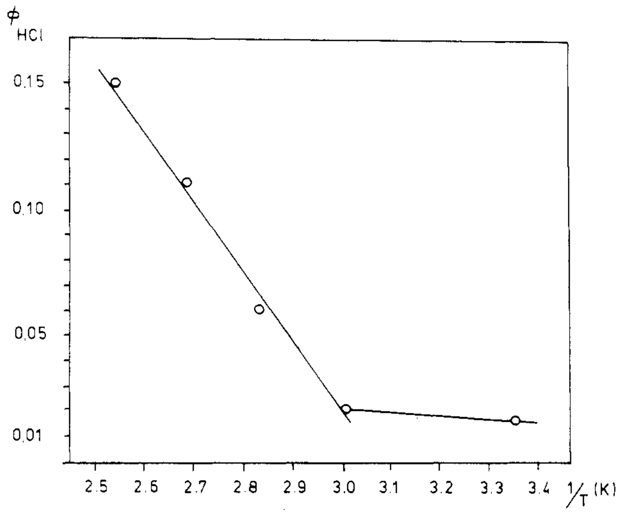


Figure 6. Quantum yield of HCl evolution during photothermal dehydrochlorination of PVC.

it was previously proposed.[5,16,43]

It has been found that the quantum yield of dehydrochlorination, $\phi_{HCl} = 0.011$ in N_2 and $\phi_{HCl} = 0.015$ in oxygen, remains initially constant, while UV radiation is increasingly absorbed by the conjugated polyene sequences that are formed in the degraded polymer.[1,16,44] Determination of the quantum yield of the different processes involved in the photooxidation of PVC indicates that for each scission of the polymer backbone 11 molecules of HCl are evolved, while 3 carbonyl groups, 2 hydroperoxides, and 0.4 intermolecular cross-links appear on the polymer chain.[16,44]

The fact that the quantum yield of dehydrochlorination remains strictly constant at the beginning of the irradiation and after a few hours suggests that when UV light is absorbed by the conjugated double bond systems the initially absorbing chromophores responsible for the initiation of the degradation are mainly unsaturated structures that are always present in a commercial PVC (2–3 double bonds per 1000 monomer units).[16]

The quantum yields of dehydrochlorination measured in photothermal dehydrochlorination of PVC (Figure 6) show that two different mechanisms, which occur with different rate constants must be taken into consideration.

The constant quantum yield measured at room temperature implies that the degradation quantum efficiency is not dependent on the amount of these unsaturations in the commercial sample. When the double bonds initially present in the PVC sample were removed by catalytic hydrogenation, before induced the photooxidation, the quantum yield of dehydrochlorination remained he same, $\phi_{HCl} = 0.015$, whereas the rates of degradation and discoloration were sharply reduced.[44] The low ϕ_{HCl} value, 1.1 molecule of HCl evolved per 100 photons absorbed, indicates that most of the excitation energy is dissipated by other routes: radiationless internal conversion, fluorescence, cis–trans isomerization, and cyclization.

Polyene sequences are formed during UV and/or thermal dehydrochlorination of PVC. The initial polyenes are of different lengths and, in addition, some polyenes contain a 1,3-cyclohexadiene ring with different behavior of oxidation.[30,104,105] Interpretation of polyene bands is difficult[30,76,105–109] because of overlapping of polyene bands in the region of 250–300 nm with the bands of oxygen-containing groups such as CO, CHO, and —O—C=O and because of the formation of polyene–HCl charge-transfer complexes[89] with strong displacement of the absorption band from the UV to the visible range. Polyene sequences observed from derivative spectra can be a result of the presence of unsaturation: at the end, in the middle, at a branch point, and starting and ending at a branch point in the polymer chain. The presence of these structures may lead to four distinct absorption species for each value of *n*. The alkyl group attached to any polyene causes a bathochromic shift of 5 nm, irrespective of the value of *n*. The absorption derivative spectroscopy (Figure 2) shows very accurately the positions of new bands for polyene structures with different *n*. Positions of these bands agree with positions of bands obtained from absorption spectroscopy by Daniels and Rees.[76]

The UV irradiation causes formation of polyene structures that are concentrated in a thin layer at the surface.[18,110] As the polyenes strongly absorb, this layer can act as a protective skin that prevents subsequent photodegradation of the internal zones. This hypothesis has been rejected by Verdu,[89] who measured high transmission of UV (>80%) through samples. This invalidates the hypothesis of the high concentration of polyene close to the exposed surface.

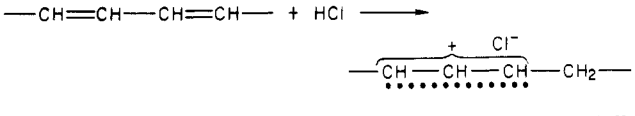
The rate of propagation and consequent polyene sequence length are also enhanced by syndiotactic arrangements, since polymers with high syndiotactic content produce abnormally long polyene sequences.[111]

A photochemical process must take place between polyene sequences and HCl upon irradiation of PVC at wavelengths >300 nm.[18] The most likely reaction consists of a photoaddition of HCl onto polyenes, as suggested by Owen and Williams,[101–103] in order to account for the observed photobleaching of thermally degraded PVC in the presence of HCl. These addition reactions were assumed to be reversible by consideration of the photostationary state that is reached after extended irradiation time. A very efficient photoaddition of HCl onto the polyenes with sequence length between 3 and 8 occurs. During this process a redistribution of the polyene sequence length occurs.[5,6,20,23,31,101] Even when HCl was thoroughly removed, some photobleaching was observed, probably owing to a cage reaction between evolved HCl and an adjacent polyene.[18] Consequently, the slow increase in HCl evolution at the beginning of UV irradiation and/or heating of PVC samples can be expected to be the result of reverse reaction of HCl with polyene sequences. HCl appears to be a product of PVC degradation that is difficult to separate from the degraded PVC.

Oxygen[6,70,112,113] and singlet oxygen[113] also react with polyene structures. Bleaching in the dark is caused by the reaction of molecular oxygen with free electrons delocalized (solitons) in the longer polyenes. Such reactions split the polyenes and produce shorter sequences.

The presence of certain metal ions, notably Fe^{3+} and Zn^{2+}, generates an additional color, characterized by strong absorption in the red region (500–800 nm) of the spectrum.[114] Fluorescence measurements confirm that the species responsible for the colors are rapidly dissociated in THF, leaving polyene sequences closely related to those formed in the absence of metal ions. The presence of HCl, which is also a primary product, is necessary for the efficient generation of the color.[114]

Other types of species responsible for a color could be one of the three closely related types: (i) carbenium ion type complexes,[103]



$$—CH{=}CH—CH{=}CH— + HCl \longrightarrow —\overbrace{CH—CH—CH}^{+\quad Cl^-}—CH_2—$$

(ii) charge-transfer complexes between polyenes in partially degraded PVC and halogen atoms or molecules,[115]

$$\text{polyene} + \text{Hal}_2 \rightarrow (\text{polyene}^+\text{Hal}_2^-)$$

and (iii) Friedel-Crafts type π complexes between polyenes in thermally degraded PVC and metal chlorides formed by the effect of HCl on metal stearate stabilizers.[116]

The rapid dehydrochlorination observed during photothermal decomposition of PVC (Figure 4) can be explained by the following mechanism proposed by us. Below T_g (87 °C for PVC) chain segments are frozen in fixed positions in a disordered quasi-lattice. Some molecular movements of PVC chain segments take place in the form of vibrations about a fixed position. A diffusional rearrangement of the segmental position is less probable. With increasing temperature, the amplitude of segmental vibrations increases. In the transition state, chain segments have sufficient energy to overcome the secondary intramolecular bonding forces. In the rubbery state of PVC the segmental motions are very rapid, whereas the molecular motion (the motion of entire molecules) is restricted by chain entanglements. With increasing temperature the degree of entanglements decreases and the molecular slip increases. If HCl molecules are evolved during the photo- and/or thermal dehydrochlorination of PVC below T_g, they are mostly retained in the polymer matrix because of limited motion between macromolecules of PVC that are in fixed positions. These HCl molecules probably react with double bonds formed during UV and/or thermal degradation, as has been proposed by Owen and Williams.[101-103] With increasing temperature, diffusion of HCl molecules out of the PVC sample increases and the probability of their reaction with polyenes decreases. But this mechanism cannot simply explain rapid evolution of HCl during photothermal dehydrochlorination of PVC. We proposed a new insight for that mechanism. With increasing temperature thermal excitation of a given bond increases, e.g., C–Cl (vibrational energy of a bond increases). If the energy of excitation is higher than the energy of dissociation of the C–Cl bond, the formation of polymer alkyl and chlorine radicals occurs. If molecules with an increased vibrational energy absorb light, the electronic-to-vibrational energy transfer occurs, and in this moment a given bond has enough excess energy to dissociate into free radicals. We observed an effect of addition of two types of energy: thermal energy and energy from the light quanta; the latter was also observed and reported by Reinish et al.[117] It is quite probable that most of the fluorescence-emitting groups formed during photodegradation (Figure 3b) dissociate into free radicals by the proposed electronic-to-vibrational energy transfer, which can be observed from the comparison of part a of Figure 3 with part b. More detailed studies on the photothermal dehydrochlorination of PVC should give a lot of new ground on the initiation mechanism of PVC degradation.

Acknowledgment. These investigations are part of a research program on the photodegradation of PVC supported by the Swedish National Board for Technical Developments (STU), which we gratefully acknowledge.

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Polymers and Copolymers of Imidazole-Containing Isocyanides. Esterolytic Activity and Enantioselectivity[1]

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ABSTRACT: Rate constants have been measured for the hydrolysis of nitrophenyl and dinitrophenyl esters catalyzed by imidazolyl-containing polymers and copolymers of isocyanides, $[\mathrm{R{-}N{=}C{<}}]_n$. The isocyanides R—N=C were derived from L- (and D-) alanyl-L-histidine, L-alanyl-L- (and D-) serine, L- (and D-) alanyl-L-histidyl-L-serine, and L-alanyl-L-histidyl-D-serine. Active species are the neutral imidazolyl groups. Generally, the polymers show markedly higher activities than corresponding low molecular weight compounds. This enhancement in activity is ascribed to cooperative effects involving interactions of imidazolyl with neighboring imidazolyl and carboxylate groups. The activities are appreciably higher in the presence of positively charged surfactants. This effect is ascribed to the formation of a hydrophobic pseudophase by arrangement of surfactant molecules around a negatively charged polymer molecule. Enantioselectivities have been determined in the hydrolysis of two chiral amino acid esters. In the presence of surfactant, k_L/k_D values up to 2.94 have been obtained.

Introduction

The development of new catalysts after the example of enzymes in nature is currently a topic of main interest.[2] Many studies are dealing with catalytic systems that mimic proteases. The reason for this choice is that the principles of protease action have been studied extensively and are now starting to be understood.[3] For the construction of an artificial proteolytic catalyst the following features are thought to be required:[3d] (i) a nucleophile and a proton transfer system; organized to complement the structures of the amide or ester substrate; (ii) a water-soluble chiral frame to anchor the catalytic functions and to provide a binding site; and (iii) a hydrophobic microenvironment to mimic the hydrophobic interior of a protein.

The realization of all these features is difficult to achieve. Substantial progress, however, has been made in both low

0024-9297/85/2218-1818$01.50/0