Structure and Degradation of Commercial Poly(vinyl chloride) Obtained at Different Temperatures

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ABSTRACT: The influence of microstructure on thermal degradation behavior was studied for four commercial poly(vinyl chloride) (PVC) resins with different polymerization temperatures and for two low molecular weight fractions. The samples were characterized by determining tacticity and the content of labile chlorine, i.e., internal allylic and tertiary chlorine. The degradation rates were measured both in nitrogen and in an atmosphere containing HCl, and the polyene sequence distributions were monitored by UV–visible spectroscopy. It was found that there is a strong relation between the content of labile chlorine and the dehydrochlorination rate in nitrogen. For tacticity, on the other hand, the relation is much weaker. When degradation was performed in an atmosphere containing HCl, the dehydrochlorination rate was increased and the polyene sequence distribution was shifted toward longer polyenes. It is concluded that labile chlorine contributes most to the initial degradation rate and that tacticity is of minor importance. Furthermore, the presence of HCl in the sample, which depends on the dehydrochlorination rate, is an important factor determining the degradation behavior.

Introduction

Over the years many attempts have been made to understand the degradation behavior of poly(vinyl chloride) (PVC). Most of them have dealt with irregular structures in the polymer, e.g., initiator residues, unsaturated chain ends, internal unsaturation, branches, head-to-head structures, and oxidation structures.[1–4] There has been considerable controversy concerning the nature, concentration, and relative importance of these anomalous structures in the polymer. In our work with polymers prepared at reduced monomer pressure we have been able to establish a correlation between the rate of dehydrochlorination and the amount of tertiary and internal allylic chlorine.[5–7] According to our results, the more frequently occurring tertiary chlorine is the most important labile structure in PVC. We have also studied thermal degradation of PVC with increased heat stability, obtained by modification and by anionic polymerization.[8–10] It was shown that treatment with Me_3Al to a large extent removed labile chlorine and that the dehydrochlorination rate decreased to approximately 20% of that of unreacted PVC. Minsker et al. have claimed that internal unsaturation is oxidized to ketoallylic groups. They consider this group to be the most important defect for initiation of the thermal degradation of PVC.[11]

Nowadays, there is also strong support for the existence of random dehydrochlorination, i.e., initiation at the ordinary units.[7,12–15] In a series of papers, Millan et al. have studied the influence of tacticity on the thermal stability of PVC.[16–27] They have argued that GTTG$^-$ isotactic and TTTG heterotactic triads are susceptible to thermal dehydrochlorination. Furthermore, they have argued that the polyene sequence distribution markedly depends on the tacticity of the polymer. It should, however, be emphasized that both the content of labile defects and the stereostructure are changed by varying the polymerization temperature. We therefore consider that the conclusions drawn by Millan et al. are questionable.

Although several papers have dealt with the influence of labile defects and the influence of tacticity on the thermal degradation of PVC, this work is the first experimental attempt at differentiating between the two structural features. We will mainly discuss the influence of microstructure on the degradation behavior of four commercial PVC resins with different polymerization temperatures.

Experimental Section

Materials. Four commercially available polymers were used in the present investigation: Pekevic S-83 (I), Pevikon S-687 (II), Vestolit S 8054 (III), and Vinnol 315/100 (IV). The fractions of samples I (I-S) and IV (IV-S) were obtained by extraction with acetone (15 g of PVC/500 mL of acetone) at 20 °C over a period of 20 h. After filtration, the soluble polymer was precipitated with methanol, washed with fresh methanol, and vacuum dried at room temperature.

Thermal Degradation. Thermal degradation experiments were performed with two different types of apparatuses. A Perkin-Elmer TGS-2 was used to measure the weight loss of the PVC samples during degradation in HCl/nitrogen (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. Degradation experiments were also performed in a specially designed apparatus described earlier.[28] 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 a 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 rate of dehydrochlorination is expressed as evolved HCl, as a percentage of the theoretical amount, per minute.

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 tetrahydrofuran.[29]

Molecular Weight Distribution. Size-exclusion chromatography (SEC) and viscometry were used to determine the molecular weight distribution. A Waters Associates GPC Model 200 operating at 25 °C with THF as solvent was used. The column combination consisted of five Styragel columns with permeabilities ranging from 10^3 to 10^7 Å, giving good separation in the molecular weight range of interest. The intrinsic viscosity was determined with a SEPEMA on-line viscometer. Details of the SEC analysis and viscometry measurements have been given

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Table I
Data for Investigated Polymers

sample	*K*-value	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
I	58	32.3	68.8
II	68	43.8	92.9
III	80	66.8	143
IV	100	80.0	712

earlier.[29] To calculate molecular weight averages, the computer program devised by Drott and Mendelson[30] was used.

Determination of Internal Double Bonds. The number of internal double bonds (or sequences) in the samples was determined by following the changes in M_n caused by the ozone oxidative cleavage of all double bonds. The ozonolysis was principally performed according to Michel et al.[31] PVC (500 mg) was dissolved in cyclohexanone (100 mL), and a small amount of methanol was added to facilitate the cleavage of the ozonide formed. The ozonolysis was performed at −20 °C for 2 h, and the polymer was recovered by precipitation in methanol and dried in vacuum 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) the oxidative treatment:

$$(C{=}C)_n/1000VC = (1/M_n - 1/M_{n,0})(62500)$$

The number of internal double bonds was also determined by ^{1}H-NMR according to Darricades-Llauro et al.[32] Spectra were obtained with a Varian XL-300 spectrometer. The samples were observed at room temperatures as 5% solutions in THF-d_8. The number of internal double bonds was calculated from the difference between the total number of olefinic protons and the chloromethylic protons of the unsaturated end group ($-CH_2-CH{=}CHCH_2Cl$).

Determination of Branches. The branch structures were determined by ^{13}C-NMR after reduction. The reductive dechlorinations were performed in a mixture of tetrahydrofuran and xylene with Bu_3SnH as reducing agent. The experimental details have been given earlier.[33] Proton-decoupled ^{13}C-NMR spectra were obtained with a Varian XL-300 spectrometer. The reduced samples were observed at 110 °C as 10–15% (w/v) solutions in 1,2,4-trichlorobenzene with 20% benzene-d_6 to provide the deuterium lock. The acquisition time was 2 s, the tip angle 60°, and the pulse delay 8 s. The number of scans accumulated was 7000–8000.

Determination of Tacticity. The tacticities were measured from ^{13}C-NMR spectra recorded on a Varian XL-300 spectrometer. The samples were observed in mixtures of tetrahydrofuran/benzene-d_6 (volume ratio 4:1) at 50 °C. The acquisition time was 5 s, the tip angle 50°, and the pulse delay 1 s. The number of scans accumulated was 10 000.

Results and Discussion

The molecular weight characteristics of the commercially available PVC resins with different *K*-values, i.e., different polymerization temperatures, are shown in Table I. Sample IV has a much wider distribution than usually observed in PVC. The MWD is however symmetrically broadened, which indicates that the temperature has varied over a relative wide range. Unfortunately, the recipes, temperatures, and conversions are not known. These data are however, of minor importance, since the aim of the work was to study the influence of structural defects compared with the influence of tacticity on the thermal stability of PVC. In order to investigate low molecular weight fractions, samples I and IV were fractionated by extraction with acetone (see Table II).

Table II
Data for Fractions

sample	extracted[a] from	soluble fraction (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
I-S	I	19	19.0	39.8
IV-S	IV	2.7	15.5	85.5

[a] Extraction with acetone.

Table III
Dehydrochlorination Rate at 190 °C

	% deHCl/min × 10^3	
sample	nitrogen[a]	15% HCl[b]
I	23	24
II	16_5	
III	15	26
IV	8.4	18
I-S	26	
IV-S	23	

[a] Conductometric system. [b] Thermogravimetric system.

Table IV
Tacticity of Samples

sample	[rr][a]	[mr][b]	[mm][c]
I	0.314	0.495	0.191
II	0.333	0.483	0.184
III	0.332	0.495	0.173
IV	0.332	0.492	0.176
I-S	0.299	0.503	0.198
IV-S	0.319	0.506	0.175

[a] Fraction of syndiotactic triads. [b] Fraction of heterotactic triads. [c] Fraction of isotactic triads.

The dehydrochlorination rate in nitrogen was measured conductometrically at 190 °C. As can be seen in Table III, the rate decreases with increasing *K*-value, i.e., decreasing polymerization temperature. Moreover, the acetone-soluble fraction (I-S, IV-S) degrades at a higher rate than the corresponding whole polymer. These results are in line with the findings of Millan et al.[24] In a series of papers, they have studied nucleophilic substitution of PVC at low temperatures.[19,20,22] They found that a small fraction of the polymer (0.3–0.8%) reacted extremely fast. The degree of substitution during the fast period increased with the polymerization temperature, i.e., with increasing degree of isotacticity. It was also observed that substitution improved thermal stability. Typically, the dehydrochlorination rate was 50% lower after 0.5–1% substitution.[27] This research team considers the GTTG$^-$ isotactic triad to be the main reason for the low thermal stability.

From the results reported in Table IV, it can be seen that the isotactic content decreases from sample I to sample IV. This is caused by the difference in the activation energies for syndiotactic and isotactic placements, which leads to an increasing tendency toward isotacticity with increasing polymerization temperature.[34] Further, the acetone-soluble fractions are less syndiotactic than the whole polymers. It should be noticed, however, that the differences in tacticity are rather small. For example, the difference in the content of isotactic triads between samples III and IV is within the experimental margin of error. In their work Millan et al. have studied the influence of tacticity on thermal stability.[16–27] They found that the degradation rate of PVC depends on the overall content of isotactic triads. As shown in Figure 1, an attempt to identify some kind of correlation was not successful with the data obtained in the present investigation. However, the dehydrochlorination rate shows a tendency to increase with increasing isotacticity.

In contrast, we consider that structural irregularities are responsible for the low thermal stability of PVC. We have earlier used polymerization of vinyl chloride at pressures below the saturation value in order to produce PVC with increased amounts of defects.[5–7] We found a definite relationship between the dehydrochlorination rate and the content of tertiary and internal allylic chlorine.

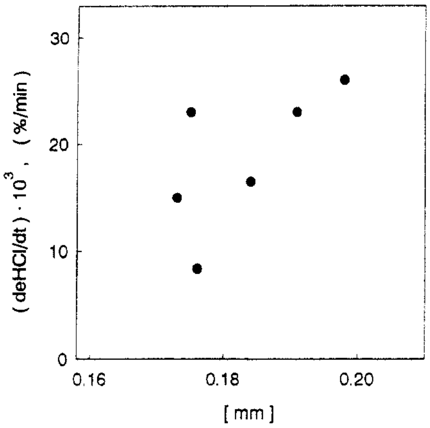

Figure 1. Relation between the dehydrochlorination rate and the content of isotactic triads.

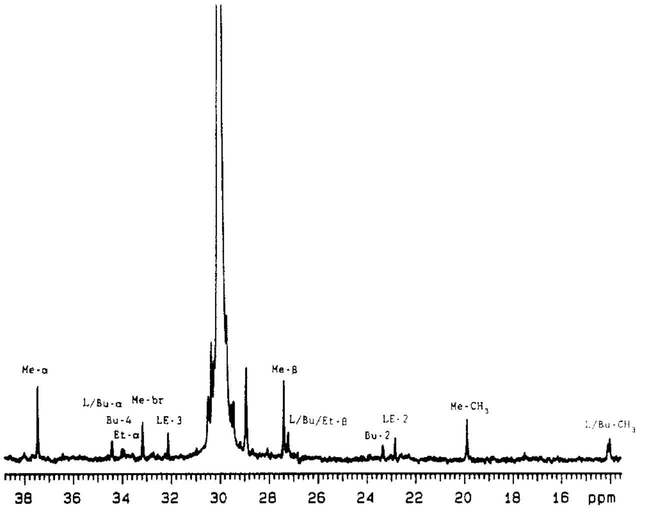

Figure 2. Proton-decoupled ^{13}C-NMR spectrum of sample I reduced with Bu_3SnH.

Table V
Content of Branches in the Reduced PVC Samples

sample	branches/1000VC methyl	ethyl	butyl	long chain	tertiary chlorine
I	4.6	0.50	1.4	0.13	2.0
II	3.5	0.31	1.0	0.11	1.4
III	3.4	0.30	1.0	0.12	1.4
IV	3.3		0.50	0.18	0.7
I-S	4.8	0.55	1.4	0.20	2.1
IV-S	3.6	0.14	1.7	0.12	2.0

The effect of these structures on the dehydrochlorination rate for ordinary PVC will be discussed below.

The branch structures of the four polymers and the two fractions were determined by ^{13}C-NMR after reductive dechlorination with Bu_3SnH as reducing agent.[33] The spectrum of sample I is given in Figure 2. The obtained spectrum shows methyl, ethyl, butyl, and long-chain branches. Table V lists the concentrations of these structures. According to our earlier results, tertiary chlorine is the most important labile defect in PVC.[7] This structure is associated with ethyl,[35] butyl,[5,35] and a major part of the long-chain branches.[5,35] As shown in Table V, the contents of ethyl and butyl branches increase from sample IV to sample I. Thus, increased temperature is favorable to the back-biting reactions that give these branches. Furthermore, the contents are higher in the acetone-soluble fraction of sample IV compared with the whole polymer. The explanation for this might be that the major part of this fraction, i.e., the low molecular weight material, is formed after the pressure drop. At this stage of the polymerization, the monomer concentration gradually decreases. This results in a lower molecular weight and a higher probability of side reactions, e.g., back-biting.

Table VI
Content of Internal Double Bonds

sample	$(C{=}C)_n$/1000VC ozonolysis	^{1}H-NMR
I	0.15	0.15
II	0.11	0.12
III	0.13	0.07
IV	0.08	0.05
I-S	0.10	0.90
IV-S	0.19	0.70

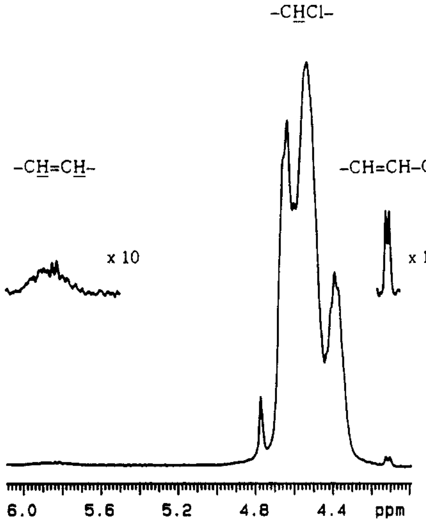

Figure 3. Part of the ^{1}H-NMR spectrum of sample I-S.

Internal allylic chlorine is another labile structure in PVC. However, the low content makes it difficult to determine this structure. An indirect measure is obtained by following the changes in M_n due to oxidative cleavage by ozone of all double bonds.[31] From the results given in Table VI, it can be seen that the contents in the original samples fall within a rather narrow interval. Recently, Llauro-Darricades et al. have studied unsaturation in PVC by ^{1}H-NMR.[32,36] They have suggested a method for determining the content of internal double bonds from the difference between the total number of double bonds and the number of pseudoterminal double bonds ($-CH_2-CH{=}CHCH_2Cl$) (see Figure 3). For the virgin samples, the contents of internal double bonds obtained by ^{1}H-NMR are well in agreement with those from ozonolysis (see Table VI). For the extracts, on the other hand, the values obtained using the ^{1}H-NMR method are much higher. In the case of ozonolysis, the determination of M_n is a crucial point. Using SEC the precision is high (2–4%)[37] and should, in principle, not depend on molecular weight. The uncertainty means that the double bonds in the outermost part of the chains are not determined. For low molecular weight polymer, e.g., the fractions of samples I and IV, it must be remembered that dn/dc depends on molecular weight.[38] This could influence the calculation of M_n and thus also the determination of internal double bonds. Furthermore, for the fractions, ozonolysis may produce material which could be lost during precipitation due to low molecular weight. This leads to an underestimation of the number of internal double bonds, and we have therefore used the values obtained by ^{1}H-NMR.

The content of internal double bonds shows the same behavior as for the branches, i.e., a higher content in polymers obtained at high temperatures and in the low molecular weight fraction of sample IV. In Figure 4 the content of labile chlorine is taken as the sum of the tertiary and the internal allylic chlorine. The figure shows that

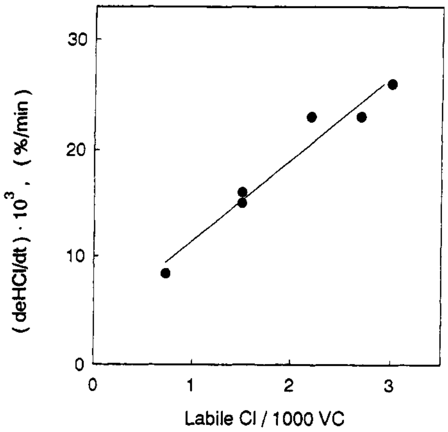

Figure 4. Relation between the dehydrochlorination rate and the content of labile chlorine.

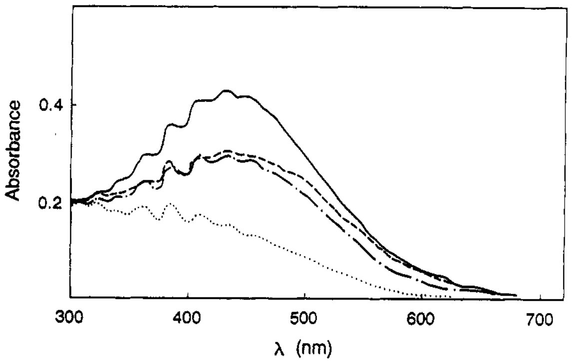

Figure 5. UV–visible spectra for samples degraded at 190 °C in nitrogen: sample I (—), II (– · –), III (- - -), and IV (· · ·). All samples were degraded to 0.2% HCl.

there is a strong relation between the dehydrochlorination rate and the content of labile chlorine for the four conventional PVC samples and the two fractions. It should be emphasized that these samples are "ordinary". This means that the contents of defects are low compared to that of PVC obtained at subsaturation conditions.[7] The relative reactivity of the two structures has been the subject of much discussion (see, e.g., ref 3). Our previous work indicated that the reactivity is of the same order.[6] We therefore consider that the effect of the less frequently occurring internal allylic chlorine is of minor importance in whole polymers.

The results above show that the dehydrochlorination rate increases both with the content of isotactic triads and with the amount of labile chlorine. It is, however, obvious that labile chlorine associated with defects plays the most important role for the dehydrochlorination rate. As an example, a comparison between sample IV and the acetone-soluble fraction, IV-S, reveals that the degradation state is 3-fold higher for the latter. Since the isotacticity is almost the same, the difference can be related to the higher content of labile chlorine in sample IV-S, 0.75 compared to 2.7/1000VC.

UV–visible spectroscopy was used to investigate the polyene sequence distribution. Many attempts have been made to evaluate the spectra of degraded PVC in terms of polyene sequence distribution. Braun and Sonderhof have shown that the spectra are put together in a complicated way by superposition of several absorptions of individual polyenes.[39] It is however clear that the maximum absorption wavelength increases with increasing length of the polyenes. The spectra of samples I–IV degraded to 0.2% HCl loss are shown in Figure 5. Sample I has a high absorption at higher wavelengths; i.e., the polyene sequences are relatively long. Sequence lengths of this magnitude give highly discolored materials. The polyene distribution in sample IV is markedly shifted toward shorter sequences. Obviously, the average polyene sequence length tends to increase with increasing dehydrochlorination rate. Considering our earlier work[8–10] on modified PVC and HCl catalysis, it is likely that the increased length of the polyenes can be related to a higher stationary concentration of free HCl.

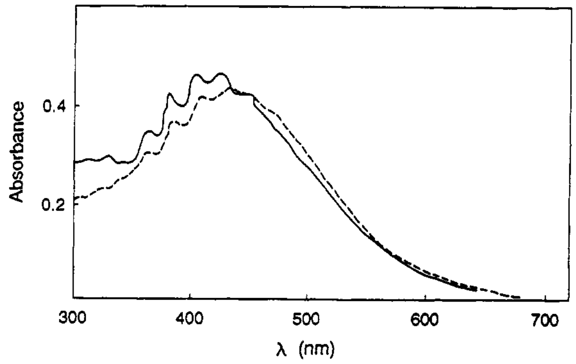

Figure 6. UV–visible spectra for sample I degraded at 190 °C in nitrogen (—) and in HCl (- - -). Both samples were degraded to 0.2% HCl.

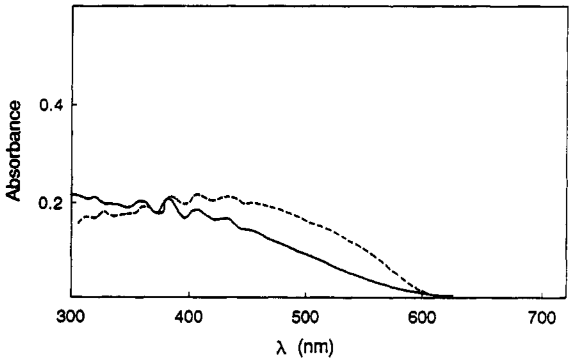

Figure 7. UV–visible spectra for sample IV degraded at 190 °C in nitrogen (—) and in HCl (- - -). Both samples were degraded to 0.2% HCl.

In order to elucidate the influence of HCl, degradation experiments were performed in nitrogen containing 15% HCl. For sample I, adding HCl did not affect the degradation behavior, (see Table III and Figure 6). This is probably because a high level of HCl is reached during degradation due to a high dehydrochlorination rate, i.e., the HCl generated is sufficient to obtain maximal catalysis of the propagation step of the dehydrochlorination. For sample IV, on the other hand, the dehydrochlorination rate is higher and the polyene sequence distribution is shifted toward longer sequences for degradation in an HCl atmosphere compared with degradation in nitrogen (see Figure 7). Interestingly, PVC with a low polymerization temperature (sample IV) and PVC with an enhanced thermal stability, e.g., PVC obtained by polymerization with butyllithium as initiator and PVC that has been reacted with tin carboxylate,[8–10] exhibit similar behavior during degradation. This supports the idea that the polyene sequence distribution depends on the HCl concentration in the sample.

Contrary to the theory above, Millan et al. have argued that tacticity, especially isotactic sequences, influences the polyene propagation.[17,18,21,27] This could per se explain the differences between the spectra in Figure 5. However, since both tacticity and the content of defects change with the temperature, this explanation must be questioned. In a recent work we have alkylated an ordinary suspension PVC, obtained at the same polymerization temperature as sample II, with trimethylaluminum.[10] It was shown that the dehydrochlorination rate was reduced to 20% of

Table VII
Tacticity of Untreated and Alkylated PVC

sample	[rr]	[mr]	[mm]
untreated	0.328	0.492	0.180
alkylated	0.326	0.491	0.183

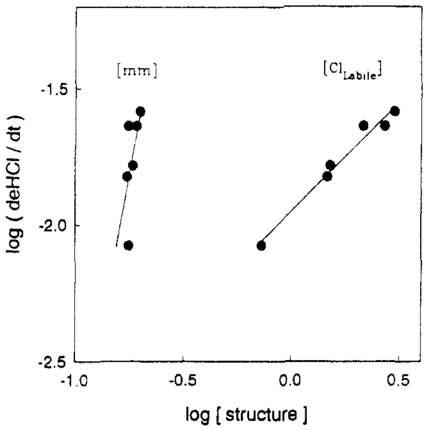

Figure 8. Correlations between the rate of dehydrochlorination and labile chlorine and isotactic triads, respectively, following the relation log (deHCl/dt) = constant + a log [structure].

that of unreacted PVC and that the treatment to a large extent removed tertiary and allylic chlorine. The total degree of substitution was quite low, on the order of 0.1 mol %. This implies that substitution of secondary chlorine, which would create terminating sites for zipping dehydrochlorination, was very limited, if it occurred at all. It should also be pointed out that the degree of substitution was considerably lower than the content of GTTG⁻ isotactic triads.[24,26] As shown in Table VII, the alkylation did not change the stereostructure. The decreased dehydrochlorination rate can thus be related to the low content of labile chlorine. Besides the decreased rate of dehydrochlorination, the alkylated sample gives a lower content of long polyenes when degraded. The alkylated PVC and sample IV thus exhibit similar degradation behavior. The tacticities, on the other hand, are different. Hence, it is reasonable to believe that the concentration of HCl in the sample, which depends on the dehydrochlorination rate, is a major factor determining the polyene sequence distribution, and it seems most likely that tacticity is of minor importance.

According to our opinion, the results thus support our idea that the labile chlorine in irregular defects, such as branches and double bonds, is more important than the isotactic sequences in determining the degradation pattern of PVC. It should, however, be stressed that these structural features change simultaneously with the polymerization temperature. In an attempt to model the dependences on the structural features, the following expression can be used: deHCl/dt = (constant) [structure]^{a}. The relevant data are plotted in a log–log plot in Figure 8. For both labile chlorine and isotactic triads a linear relation is obtained. An evaluation of the plot gives $a = 1$ for labile chlorine and $a = 5$ for isotactic triads. Although these values should be treated with caution, it can be noted that $a = 1$ is quite reasonable but that $a = 5$ is much too high. This further supports our view on the importance of labile chlorine. Any influence of tacticity should, however, not be ruled out completely, in particular with respect to random initiation and the length of the polyene sequences. This would, of course, to a certain extent also influence the rate of dehydrochlorination.

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