

On the Influence of HCl on the Thermal Degradation of Poly(Vinyl Chloride)

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Synopsis

The thermal degradation of PVC was studied at 190°C in pure nitrogen and nitrogen containing 10, 20, and 40% HCl (by volume). The rate of dehydrochlorination was determined by gravimetry. Degradations in nitrogen were followed with conductometry in addition. Changes in molecular weight distribution and degree of long-chain branching (LCB) were determined by gel permeation chromatography-viscometry and polyene sequence distribution by UV spectroscopy. The rate of dehydrochlorination increases with the HCl content of the atmosphere. The rate of molecular enlargement also increases but only as a result of the increased dehydrochlorination rate. The increase in \bar{M}_w and LCB are thus related to the extent of conversion only. Changes in the UV spectra indicate that the increase in rate of dehydrochlorination is mainly due to increased propagation rate in atmospheres containing less than 10% HCl. At higher HCl contents an increase in initiation rate is noted. It is suggested that this, at least in part, is due to the fact that HCl, by forming a cyclic transition state, catalyzes the random elimination of HCl. This process, in turn, is promoted by the presence of polyene sequences.

INTRODUCTION

Over the years the role of HCl in thermal degradation of poly(vinyl chloride) (PVC) has been a matter of dispute. Although a few research workers have recently reported that HCl has no catalytic effect under inert conditions,^{1,2} there is nowadays overwhelming experimental evidence that HCl does catalyze the thermal degradation of PVC, both in the presence of oxygen and under inert conditions.³⁻⁵ Little is known, however, about the mechanisms by which such an effect is achieved. The elucidation of this is of great importance, e.g., for the development of efficient heat stabilizers for PVC.

It is obviously difficult to design experiments which discriminate between the effect of HCl on the initiation, propagation, and termination steps in dehydrochlorination of PVC. Minsker et al.⁶ used kinetic measurements on the dehydrochlorination. They concluded that the increased rate in the presence of HCl was due to an increase in the propagation rate. In a few investigations, molecular changes have also been determined. Marks et al.⁷ measured the rate of formation of insoluble material during heating of bulk samples in the presence of either nitrogen or HCl. They stated that HCl enhances crosslinking. Thallmaier and Braun⁸ compared the changes in the UV visible spectrum of PVC when degraded in nitrogen as a film or in bulk and related the differences to the different HCl contents within the samples. They concluded that the observed tendency towards longer polyene sequences in film samples was due to a higher HCl content. Carezza et al.⁹ found the opposite effect in similar experiments.

In the present work changes in molecular-weight distribution (MWD), degree

of long-chain branching (LCB), and polyene sequence distribution have been studied during thermal degradation of PVC in nitrogen containing (0–40)% HCl (by volume). The extent of dehydrochlorination was determined by gravimetry. In pure nitrogen, conductometric measurements were used in addition.

EXPERIMENTAL

Materials

A commercial suspension PVC was used (Pevikon S 707, KemaNord AB, Sweden). This quality was formerly designated Pevikon R 24. Polymer characteristics: $\bar{M}_w = 125,000$, $\bar{M}_n = 55,000$, methyl content is 5.1/1000 C (ref. 10), and internal double bonds are 0.05/1000 C.¹⁰ Tetrahydrofuran (THF) of puriss grade was purified as described earlier.¹⁰ Nitrogen of high purity (<10 ppm O₂) and nitrogen with 40% HCl was used.

Thermal Degradation

The degradation experiments were performed in a specially designed apparatus described earlier.¹¹ As in our previous investigations on PVC degradation, bulk samples (200 mg) were heated at $190^\circ \pm 0.05^\circ\text{C}$. The atmosphere was nitrogen containing 0%, 10%, 20%, and 40% HCl which was achieved by mixing pure nitrogen and nitrogen with 40% HCl using flow meters (Rotameter). In pure nitrogen the dehydrochlorination was followed conductometrically,¹¹ while the degradation in the presence of HCl was followed by weight loss measurements using a balance with an accuracy of 0.05 mg (Mettler, Zürich, Schweiz, Model H 16). The samples were conditioned at 25°C and 65% relative humidity.

Characterization

Gel permeation chromatography (GPC) and viscometry were used for determining molecular parameters. Details of the GPC analysis and viscometry measurements have been given earlier.¹⁰ No correction for kinetic energy loss was necessary. A Waters Associates GPC Model 200 operating at 25°C with THF as solvent was used. The column combination consisted of 5 Styragel® columns with permeabilities ranging from 10^3 to 10^7 Å, giving good separation in the molecular weight (MW) range of interest.

To calculate MW_D , average MW's, and LCB from the GPC and viscometric measurements, the computer program devised by Drott and Mendelson¹² was used, assuming tetrafunctional branch points. The calibration for linear PVC was obtained via the universal calibration curve as described earlier.¹⁰

The amount of insoluble material (gel content) was taken as the amount of material not passing a filter (Kruger) of $0.5 \mu\text{m}$ pore size after dissolving the sample in THF at 120°C for 3 hr.¹⁰ UV visible spectra were recorded on solutions in peroxide-free THF¹⁰ using a Beckman DK 2 A spectrophotometer.

RESULTS AND DISCUSSION

It is generally agreed⁴ that the nominal PVC structure is quite stable towards thermal dehydrochlorination and that the relatively low thermal stability of conventional PVC is due to irregular chain structures resulting in a weakening of C—Cl bonds.¹³ Among such weak structures internal allylic C—Cl bonds are considered to be the weakest¹⁴ followed by tertiary C—Cl bonds. The amount of internal allylic chlorine is quite low, of the order of 0.05/1000 C.¹⁵ No tertiary chlorine has so far been detected which means that the content should be less than 1/1000 C,¹⁶ taking the relatively low sensitivity of the analytical methods into account.

Minsker et al.¹⁷ pointed out that a random elimination of HCl from regular monomeric units also should be considered. They found the rate constant for this process to be about four orders of magnitude lower than the rate constant for the growth of polyene sequences. Recently, Nolan and Shapiro¹⁸ also discussed a random elimination of HCl.

In accordance with Minsker et al. we prefer to consider this formation of isolated double bonds to be the *initiation* step of the thermal degradation. Irrespective of the nature of the starting point, an allylic structure results after the first intrachain elimination of a HCl molecule. Dehydrochlorination then *propagates* through a rapid series of HCl elimination steps forming polyene sequences,² the so called "zipper" reaction. The *termination* of the dehydrochlorination chain reaction is not clearly understood. One important path for termination is supposed to be via interchain reactions leading to crosslinking.^{4,10}

Rate of Dehydrochlorination

An accurate determination of the rate of dehydrochlorination can be made conductometrically as reported elsewhere.¹¹ For obvious reasons this method can not be used when the carrier gas contains HCl. Various means of following the dehydrochlorination in such systems have been applied, e.g., by measuring the increase in pressure¹⁹ or the increase in absorbance in the UV visible range.⁷

Under inert conditions and at temperatures below 200°C, HCl is essentially the only low molecular weight material formed. Trace amounts of aromatic compounds, mainly benzene, are also formed.²⁰ Also in the presence of HCl, the formation of benzene remains negligible.²¹ We therefore chose to determine the weight loss as a measure of dehydrochlorination. Such determinations on samples degraded in pure nitrogen have been correlated to the HCl loss determined conductometrically. The rate of conversion has been calculated in the following way.

First a series of degradations were carried out in pure nitrogen and the times to reach different conversion X_{N_2} in the range (0.3–2.5)% of the theoretical amount of HCl in PVC were determined conductometrically. The weight loss was also determined and was found to be systemetrically 0.5 mg (of the 200 mg sample) higher than the weight loss calculated from the conductometric measurements. This could be due to difficulties in obtaining the same moisture content when weighing the samples before and after heat treatment. To correct for this discrepancy the primary weight loss data have been reduced with 0.5 mg.

TABLE I
Corrected Weight Losses in mg

HCl (%)	Degradation time (min)	84	126	168	210
	X_{N_2} (%)	1.0	1.5	2.0	2.5
0		1.2	1.75	2.34	2.92
10		1.4	2.8	4.8	6.2
20		1.6	3.3	6.1	11.7
40		2.5	6.7	11.3	22.0
		3.0	7.1	12.1	22.7

Using the predetermined time levels giving known X_{N_2} values in the range (1–2.5)% degradations were also performed in atmospheres containing 10%, 20%, and 40% HCl and the weight loss were determined gravimetrically. Shorter degradation times were omitted as the weight loss was too small to be determined accurately. The corrected data are given in Table I and Figure 1. The corrected weight loss data were then converted to corresponding values of conversion X . The relation between conversion and HCl content of the atmosphere was found to obey the following equation

$$X = X_{N_2} + 3.13X_{N_2}^{2.75} V_{HCl} \quad (1)$$

where V_{HCl} is volume fraction of HCl. In Figure 2 the good agreement with the observed data is illustrated. The equation is similar to that suggested by Troitskaya et al.²² and shows the strong accelerating effect of HCl on the dehydrochlorination of PVC.

Molecular Enlargement

Due to rapidly increasing gel formation at conversions higher than about 1.5% meaningful MW data could be determined only below this level. In Figure 3 the changes in MW_D after 59 min of degradation are shown. For this time all HCl levels are represented and the behavior is representative for the other time levels. It is obvious that the changes in MW_D are also strongly dependent on

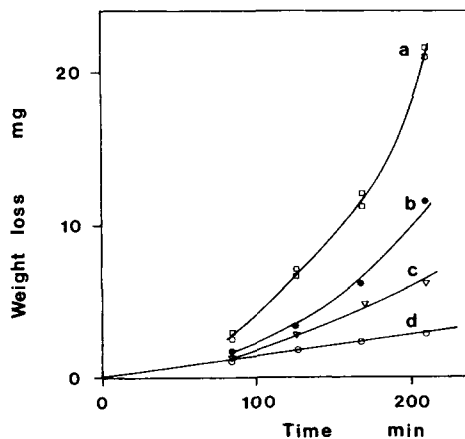


Fig. 1. Relation between weight loss and degradation time at different HCl contents: (a) 40% HCl, (b) 20% HCl, (c) 10% HCl, (d) pure nitrogen.

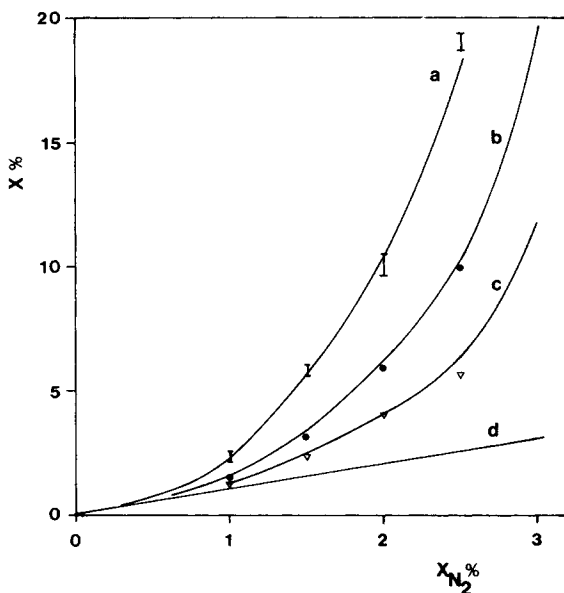


Fig. 2. Relation between X and X_{N_2} at different HCl contents. Comparison between data points and eq. (1) (—), (a) 40% HCl, (b) 20% HCl (c) 10% HCl, (d) pure nitrogen.

the HCl content in the atmosphere. With increasing HCl content an increase in the molecular enlargement reactions occurs resulting in higher MW's and LCB's (Table II). No tendency for molecular diminishing reaction was observed in accordance with our previous findings for degradation in an inert atmosphere.²³ The low \bar{M}_n and \bar{M}_w obtained for the sample heated in 40% HCl for 84 min is due to extensive gel formation (approximately 40%). Such a behavior is in accordance with our investigations on degradation of polyethylene under gelating conditions.²⁴

The increased rate of crosslinking with increasing HCl content is in good accordance with the increase in gel formation reported by Marks et al.⁷ This is not, however, evidence per se that HCl accelerates the crosslinking reactions. In order to further elucidate this point we rearranged the \bar{M}_w and LCB data in

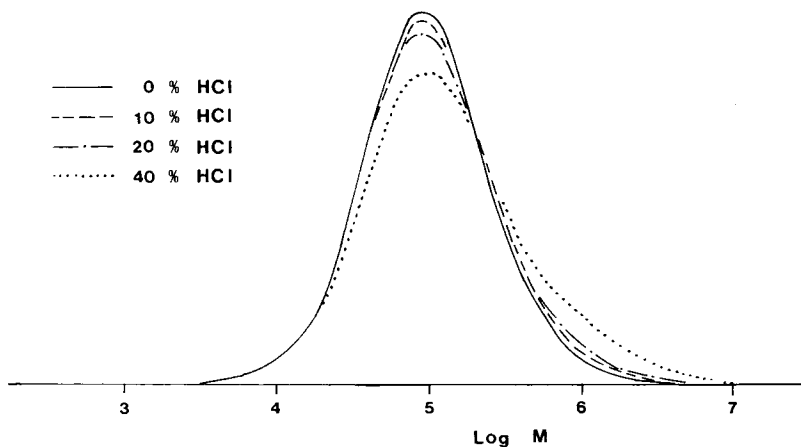


Fig. 3. Changes in MW diameter with the HCl content after 59 min of degradation.

TABLE II
Molecular Weight Averages and the Degree of Long-Chain Branching

Degradation time (min)	25.2			59			84			109		
	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	LCB ^a	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	LCB ^a	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	LCB ^a	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	LCB ^a
0	57	130	4	58	155	6.5	60	190	10	60	274	14
10	—	—	—	62	168	6	63	220	12	—	—	—
20	59	137	5	63	187	6	65	333	12	—	—	—
40	59	143	4.5	74	290	14	60 ^b	273 ^b	14	—	—	—

^a The degree of LCB is given as $\lambda \times 10^6$ where λ is the weight average number of tetrafunctional branch points per molecular weight unite.

^b Extensive gel formation.

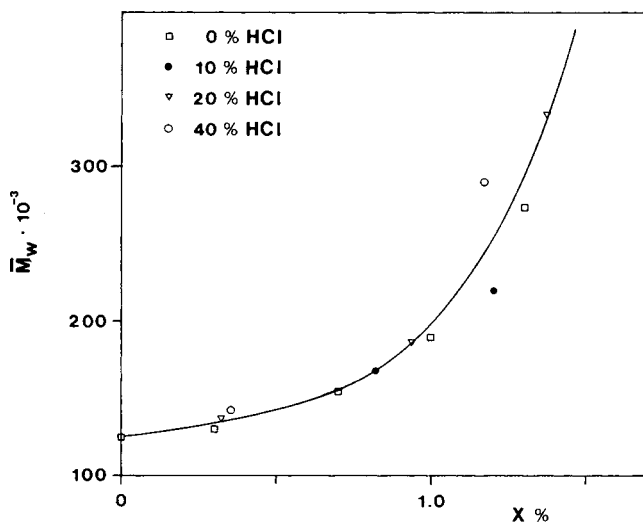


Fig. 4. Relation between \bar{M}_w and X at different HCl content.

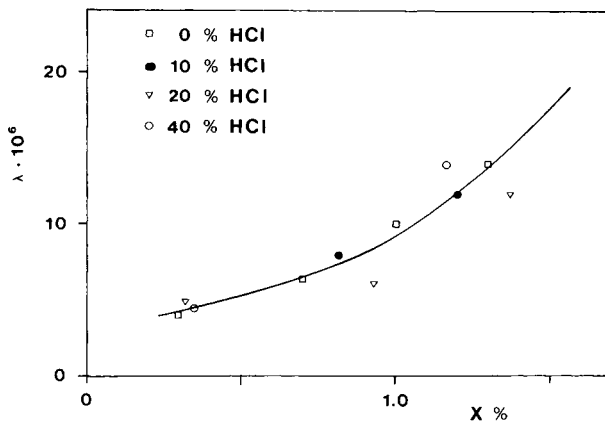


Fig. 5. Relation between LCB and X at different HCl content.

Table II according to Figures 4 and 5 where they are plotted against conversion. At the lower conversion levels, where no weight measurements were carried out, conversion X was calculated according to eq. (1). From these figures it is obvious that HCl does not catalyze the molecular enlargement reactions. Termination through crosslinking is thus related only to the extent of dehydrochlorination and independent of the HCl content in the atmosphere. Marks et al.⁷ estimated the extent of dehydrochlorination by UV visible spectroscopy. If the rate of gel formation is related to this measure instead of time, their data point to the same conclusion as reached by us.

Polyene Sequence Distributions

UV visible spectra of solutions of degraded PVC show several not very well resolved peaks which have been ascribed to certain polyene sequence lengths.^{25,26} According to Braun and co-workers it is possible to calculate the relative concentrations of the different polyenes.^{4,26} The concentration of a polyene sequence of length n can be calculated according to²⁷

$$H_n = a/m\epsilon_n$$

where a is the absorption of the solution at a wavelength corresponding to n double bonds, m is the concentration in monomeric units mole/l, and ϵ_n is the molar extinction coefficient for polyene sequence with length n . This coefficient can be calculated according to Popov and Smirnov²⁸

$$\epsilon_n = 10^4 + (n - 1) 2 \times 10^4 \text{ l/mole cm.}$$

In order to make the comparison easier, H_n is normalized with respect of H_{13} for every sample.

In Figure 6 the normalized polyene distributions of the samples degraded in pure nitrogen are plotted at different conversion. It can be seen that the relative concentrations of shorter sequence lengths increase with increasing conversion. This has been explained by an increased termination of the growing sequences due to increased crosslinking at higher conversions.^{4,10}

The samples degraded in atmospheres containing HCl show marked changes in the UV spectra. In Figure 7 the polyene distributions of samples degraded in 10% HCl are compared with those degraded in pure nitrogen. It is obvious that the presence of HCl has shifted the average sequence length towards a higher value. As the rate of dehydrochlorination increases with the HCl content, the longer sequence length observed should, at least in part, be due to an increased rate of propagation. It is not possible to state whether the initiation rate has changed. As discussed above termination through crosslinking is unaffected by HCl and is only related to the extent of dehydrochlorination. If samples degraded to the same total HCl loss in nitrogen and 10% HCl are compared, the greater amount of longer sequences in the sample degraded in the latter atmosphere implicates that fewer sequences have been formed. The greater probability for longer sequences to be terminated by crosslinking is thus demonstrated.

In Figure 8 polyene sequence distributions obtained in atmospheres containing (10–40)% HCl are given. Compared to degradations in pure nitrogen (Fig. 6) the influence of conversion is much less pronounced. At conversion higher than 0.8% no influence from the degree of conversion can be observed whatsoever.

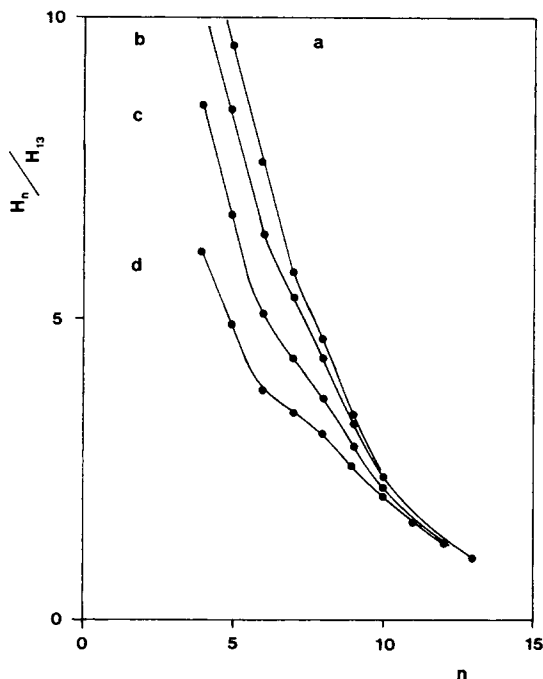
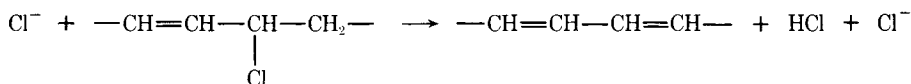


Fig. 6. Variation with conversion of the normalized polyene sequence distributions of samples degraded in pure nitrogen. Conversions: (a) $X = 1.3\%$; (b) $X = 1.0\%$; (c) $X = 0.7\%$; (d) $X = 0.3\%$.

From Figure 8 it is furthermore obvious that variations in the HCl content [in the range (10–40)%] do not influence the polyene sequence distributions. For samples with the same total HCl loss the number of sequences is therefore the same, independent of HCl content in the atmosphere. As the rate of dehydrochlorination increases with the HCl content this clearly shows that the initiation rate increases with the HCl content. This is not in accordance with the statements made by Minsker et al.⁶ (see the Introduction).

At constant conversion an increased initiation rate should, per se, result in shorter polyene sequences. The constant sequence distributions observed in our experiments imply that the rate of propagation is much higher than that of initiation. Although only observed for HCl contents higher than 10%, it is reasonable to believe that the initiation rate increases with increasing HCl content even between 0% and 10%. The rate constant for propagation appears to reach a limiting value below 10% HCl.

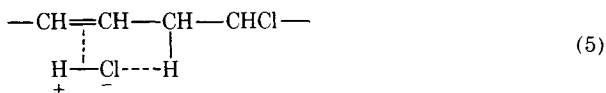
Considering the catalytic effect of HCl, some workers have proposed mechanisms for the influence of HCl on the thermal degradation of PVC. As HCl does not dissociate into radicals at temperatures lower than 200°C, Van der Ven and de Wit²⁹ proposed an ionic mechanism [eqs. (2)–(4)] to explain the catalytic effect of HCl:



or



Morikawa³⁰ suggested that HCl influences the degradation via association to a double bond as follows



Rasuvaev et al.³¹ state that the presence of polyene sequences is a prerequisite for catalytic action of HCl. They proposed a molecular mechanism [eq. (6)], an ionic mechanism [eqs. (7) and (8)] and a radical mechanism based on the addition of HCl to polyene sequences activated to the triplet stage and subsequent chain scission by homolytic cleavage. As pointed out previously we have never found any tendency to molecular diminishing reactions in thermal degradation in absence of oxygen

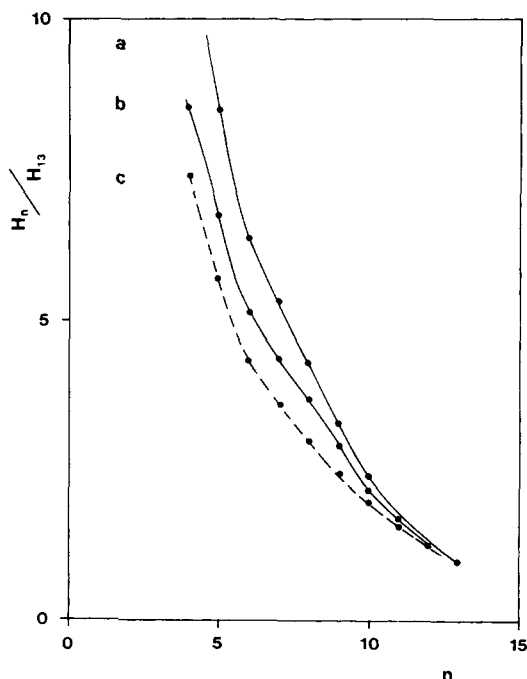
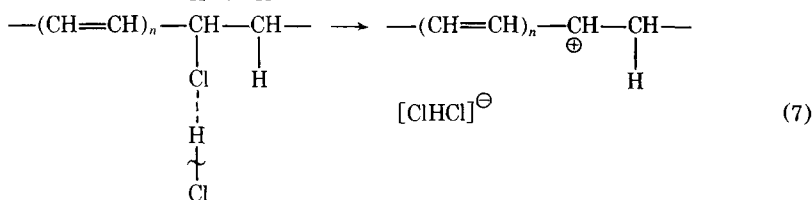
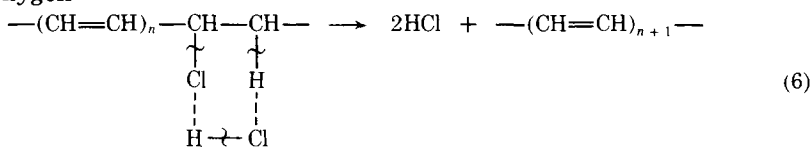


Fig. 7. Comparison between normalized polyene sequence distributions of samples degraded in pure nitrogen (—), and in nitrogen containing 10% HCl (- - -). Conversions: (a) X = 1.0%; (b) X = 0.7%; (c) X = 0.82%.

well as the autocatalytic behavior can be explained.

CONCLUSIONS

In the thermal degradation of PVC in bulk at 190°C in nitrogen containing (0–40)% HCl the rate of dehydrochlorination and the molecular enlargement increase with the HCl content. Up to 10% HCl the increase in dehydrochlorination rate is mainly due to an increase in the propagation rate. At higher HCl content an increase in initiation rate is observed. HCl does not catalyze the crosslinking reactions. At all levels of HCl content and conversion the molecular enlargement is related to the extent of dehydrochlorination only.

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References

1. I. T. Kelen, G. Balint, G. Galambos, and F. Tüdös, *J. Polym. Sci., C*, **33**, 211 (1971).
2. P. Bataille and B. T. Van, *J. Polym. Sci., A-1*, **10**, 1097 (1972).
3. W. C. Geddes, *Rubber Chem. Technol.*, **40**, 177 (1967).
4. D. Braun, *Pure Appl. Chem.*, **26**, 173 (1971).
5. G. Ayrey, B. C. Head, and R. C. Poller, *J. Polym. Sci. Macromol. Rev.*, **8**, 1 (1974).
6. K. S. Minsker, V. P. Malinskaya, M. I. Artsis, S. D. Razumovskii, and G. E. Zaikov, *Dokl. Acad. Nauk. SSSR*, **223**, 138 (1975).
7. G. C. Marks, J. L. Benton, and C. M. Thomas, *S.C.I. Monographs*, **26**, 204 (1967).
8. M. Thallmaier and D. Braun, *Makromol. Chem.*, **108**, 241 (1967).
9. M. Carenza, Yu. V. Moiseyev, and G. Palma, *J. Appl. Polym. Sci.*, **17**, 2685 (1973).
10. K. B. Abbäs and E. M. Sörvik, *J. Appl. Polym. Sci.*, **19**, 2991 (1975).
11. K. B. Abbäs and E. M. Sörvik, *J. Appl. Polym. Sci.*, **17**, 3567 (1973).
12. E. E. Drott and R. A. Mendelson, *J. Polym. Sci., A-2*, **8**, 1361 (1970); **8**, 1373 (1970).
13. D. Braun, *Degradation and Stabilization of Polymers*, G. Geuskens, Ed., Applied Science Publications, London, 1975, p. 23.
14. M. Asahina and M. Onozuka, *J. Appl. Polym. Sci., Part A*, **2**, 3515 (1964).
15. K. B. Abbäs and E. M. Sörvik, *J. Appl. Polym. Sci.*, **20**, 2395 (1976).
16. A. A. Caraculacu, E. C. Bazdacea, and G. Istrate, *J. Polym. Sci., A-1*, **8**, 1239 (1970).
17. K. S. Minsker, D. V. Kazachenko, D. V. Abdullina, R. G. Kouler, and A. A. Berlin, *Vysokomol. Soedin., Ser. A* **15**, 866 (1973); *Polym. Sci. USSR*, **15**, 974 (1973).
18. K. P. Nolan and J. S. Shapiro, *J. Polym. Sci. Symp.*, No 55, 201 (1976).
19. K. S. Minsker, V. P. Malinskaya and A. A. Panasenko, *Vysokomol. Soedin., Ser. A*, **12**, 1151 (1970); *Polym. Sci. USSR*, **12**, 1304 (1970).
20. F. Tüdös, T. Kelen, T. T. Nagy, and B. Turcsany, *Pure Appl. Chem.*, **38**, (1–2), 201 (1974).
21. M. V. Neiman, R. A. Papko, and V. S. Pudov, *Vysokomol. Soedin., Ser. A* **10**, 841 (1968); *Polym. Sci. USSR*, **10**, 975 (1968).
22. L. S. Troitskaya, V. N. Myakey, B. B. Troitskii, and G. A. Razuvayev, *Vysokomol. Soedin., Ser. A* **9**, 2119 (1967); *Polym. Sci. USSR*, **9**, 2392 (1967).
23. K. B. Abbäs and E. M. Sörvik, *J. Appl. Polym. Sci.*, **17**, 3577 (1973).
24. A. Holmström and E. M. Sörvik, *J. Polym. Sci. Chem. Ed.*, to appear.
25. A. Guyot, J. P. Benevise, and Y. Trambouze, *J. Appl. Polym. Sci.*, **6**, 103 (1962).
26. D. Braun and M. Thallmaier, *Makromol. Chem.*, **99**, 59 (1966).
27. K. B. Abbäs and R. L. Lawrence, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1889 (1975).
28. K. R. Popov and L. V. Smirnov, *Opt. Spektrosk.* **14**, 787 (1963).
29. S. Van der Ven and W. F. de Wit, *Angew Makromol. Chem.*, **8**, 143 (1969).
30. T. Morikawa, *Chem. High Polym. (Jpn.)*, **25**, 505 (1968).

31. G. A. Rasuvaev, L. S. Trotskaya, and B. B. Troitskii, *J. Polym. Sci., A-1*, **9**, 2673 (1971).
32. M. Imoto and T. Nakaya, *Kogyo Kagaku Zasshi*, **68**, 2285 (1965).
33. R. Schlimper, *Plaste Kautsch.*, **13**, 196 (1966); **14**, 657 (1967).

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