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Dehydrochlorination of Poly(vinyl Chloride) in Pyridine. II. Characterization of Dehydrochlorinated PVC

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ABSTRACT

The structural changes in PVC during thermal dehydrochlorination in pyridine have been investigated. From gel permeation chromatography analyses, chain scission and cross-linking reactions were observed. Cross-linking increased with an increase in reaction time and temperature, whereas the chain scission increased with dilution of the reaction solution. Infrared spectroscopy indicated the presence of conjugated double bond sequences in polymeric chains. Polyene sequences were analyzed by ultraviolet spectroscopy. The length of the polyene sequences and the total number of conjugated double bonds increased with reaction time. An increase in dehydrochlorination temperature lowered the fraction of long polyene sequences, and thus the discoloration. Dilution of the reaction solution decreased the polyene sequence lengths as well as the total number of conjugated double bonds. Shorter polyenes were maximum and their proportion decreased with increase in their length.

INTRODUCTION

Dehydrochlorination of poly(vinyl chloride) (PVC) is accompanied by discoloration of the product. It has been shown [1] that discoloration is essentially due to the development of conjugated double bonds (polyene sequences) formed through a "zipper" mechanism in PVC chains. A sequence of about five conjugated double bonds is required to obtain the discolored material [2]. Ultraviolet spectroscopy has been successfully applied for the evaluation of polyene sequence lengths and their distribution in polymeric chains by several workers [3-5]. Attempts have also been made to follow the molecular weight changes by the measurement of intrinsic viscosity, $[\eta]$, but no information on chain scission and molecular enlargement (branching and cross-linking) reactions could be obtained [1, 6]. Introduction of gel permeation chromatography (GPC) has facilitated the detailed studies of not only the molecular weight changes but also the changes in molecular weight distribution (MWD) [7].

Recently we reported [8] the thermal dehydrochlorination of PVC in pyridine and the effect of reaction conditions on dehydrochlorination. The present investigation deals extensively with the characterization of dehydrochlorinated PVC (DHPVC).

EXPERIMENTAL

Materials

SR-10A grade PVC supplied by Sri Ram Institute, New Delhi, India, was used. Polymer data are as follows: \bar{M}_n 43,400; \bar{M}_w 96,500; heterogeneity index (H) 2.2; $[\eta]$ (dL/g) 1.06; weight average degree of polymerization (\bar{DP}) 1544; ultraviolet spectroscopic analysis number, N, of polyenes having conjugated double bonds, n, of 2, 0.89; 3, 0.30; 4, 0.10; 5, 0.04; 6, 0.03; 7, 0.01; total number of polyenes (T_n) 1.37; total number of double bonds (D_n) 3.53; percentage of double bonds (P_n) 0.23.

Tetrahydrofuran (THF) was refluxed over sodium borohydride until no peroxide could be detected [9]. It was then distilled under nitrogen from metallic sodium. Twice distilled THF was used as the solvent for spectroscopic studies. All other reagents and solvents were of analytical grade.

Dehydrochlorination Kinetics

DHPVC was prepared by refluxing PVC in dried and distilled pyridine under nitrogen atmosphere. Details of dehydrochlorination conditions have been given earlier [8].

Viscosity Measurement

Intrinsic viscosities were measured at 30°C using an Ubbelohde viscometer. DHPVC samples were dissolved in peroxide-free THF (0.32%) under nitrogen atmosphere.

Gel Permeation Chromatography

Waters Associates GPC Model 244 was used for the determination of \bar{M}_n , \bar{M}_w , and MWD. The unit was operated with THF as carrier solvent at 25 ± 3°C using Styragel columns with pore sizes of 10⁴, 10³ and 500 Å. A flow rate of 2 mL/min and a chart speed of 0.75 in./min was maintained in all experiments. The column combination was calibrated with polystyrene standards with narrow distributions. Polystyrene calibration was transformed to PVC calibration. Approximately 0.4% solution of DHPVC in THF was prepared in all cases.

Infrared Spectroscopy

Spectra were run on PVC and DHPVC films (cast from THF) using a Unicam SP-1200 spectrophotometer.

Ultraviolet Spectroscopy

Absorption spectra of PVC and DHPVC solutions in THF were obtained by a Beckman DK-2A spectrophotometer in a 1-cm absorption cell. All the solutions (0.75 g/L) were carefully prepared under nitrogen atmosphere.

RESULTS

Molecular Weight and Molecular Weight Distribution

The molecular weight of the dehydrochlorinated PVC was evaluated by measuring the intrinsic viscosity as well as by GPC. The latter analysis also gave the MWD of the dehydrochlorinated product. From

TABLE 1. Changes in $[\eta]$ and Molecular Weight Averages with time of Dehydrochlorination: Thermal Dehydrochlorination of PVC in Pyridine (41.7 g/L) at 120°C

Dehydrochlorination time (min)	Conversion x (%)	$[\eta]$ (dL/g)	\bar{M}_n	\bar{M}_w	H (heterogeneity index)
45	2.13	0.87	38,000	85,900	2.3
90	3.42	0.63	23,500	66,800	2.8
135	3.62	0.81	37,900	109,300	2.8
180	4.53	0.82	81,100	192,100	2.4

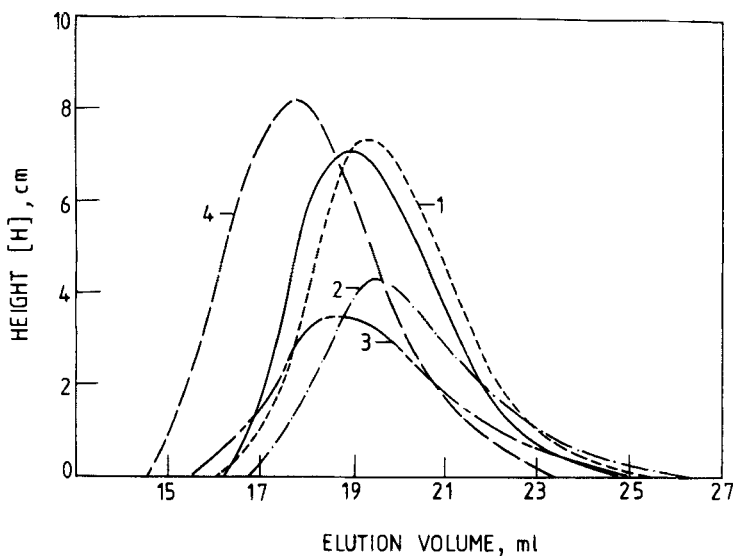


FIG. 1. Thermal dehydrochlorination of PVC in pyridine (41.7 g/L) at 120°C. Changes in MWD with dehydrochlorination time of (1) 45, (2) 90, (3) 135, and (4) 180 min. (—) PVC.

TABLE 2. Changes in $[\eta]$ and Molecular Weight Averages with Temperature of Dehydrochlorination: Thermal Dehydrochlorination of PVC in Pyridine (41.7 g/L) for 135 min

Dehydrochlorination temperature (°C)	Conversion x (%)	$[\eta]$ (dL/g)	\bar{M}_n	\bar{M}_w	$\bar{H} (\bar{M}_w/\bar{M}_n)$
120	3.62	0.81	37,900	109,300	2.8
125	3.82	0.81	59,300	117,500	2.0
135	4.14	0.81	60,600	130,900	2.2
150	5.63	0.79	32,400	80,300	2.5

the MWD curves the molecular weight averages were calculated and a comparison of these averages gave a semiquantitative measure of the molecular weight changes.

Changes in Molecular Weight and MWD with Dehydrochlorination Time

Viscosity initially dropped with an increase in reaction time but then increased continuously (Table 1).

From GPC data in Table 1 and Fig. 1 an increase in the low molecular weight fraction, and consequently a decrease in high molecular weight fraction and a shift of the distribution curve toward low molecular weight compared to that of PVC, was observed after 45 min of the reaction. From these results it is evident that chain scission reactions start at the early stages of dehydrochlorination. With an increase in reaction time (90 min) the effect became more prominent. Both \bar{M}_n and \bar{M}_w decreased, but the relative drop in \bar{M}_n to \bar{M}_w was high and as a result the value of the heterogeneity index increases. In 135 min, $[\eta]$, as well as \bar{M}_n and \bar{M}_w , increased and the MWD curve shifted to high molecular weight. The formation of an increasing amount of high molecular weight material clearly reflects the onset of cross-linking reactions. The effect became predominant with a further increase in reaction time (180 min). The increase in \bar{M}_n was higher than in \bar{M}_w , and as a result the value of H decreases.

Variations in Molecular Weight and MWD with Dehydrochlorination Temperature

Initially there was no change in viscosity with an increase in reaction temperature, but at 150°C a slight decrease in viscosity was observed (Table 2).

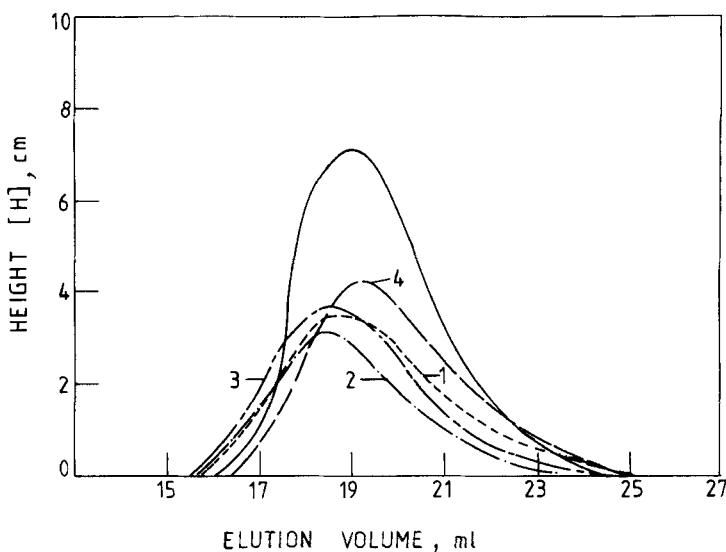


FIG. 2. Thermal dehydrochlorination of PVC in pyridine (41.7 g/L) for 135 min. Changes in MWD with dehydrochlorination temperature of (1) 120, (2) 125, (3) 135, and (4) 150°C. (—) PVC.

Substantial changes were obtained in \bar{M}_n , \bar{M}_w , and H with an increase in dehydrochlorination temperature (Table 2 and Fig. 2). DHPVC formed at 120°C showed an increase in high molecular weight fraction, a decrease in low molecular weight fraction, and a shift of the distribution curve toward high molecular weight compared to the parent PVC. The effect became more pronounced with an increase in the reaction temperature (125°C). Above 125°C the same trend continued but was not reflected in GPC data. The reason for this is that at higher temperatures, due to excessive cross-linking, much of the product separates as an insoluble mass and cannot be included in GPC studies. MWD curves for the samples prepared at 135 and 150°C showed the effect.

Variations in Molecular Weight and MWD with Concentration

The viscosity decreased continuously with dilution of the reaction solution (Table 3).

As can be seen (Table 3 and Fig. 3), a distinct decrease in \bar{M}_n , \bar{M}_w , and a continuous shift of the distribution curve toward low molecular weight was obtained with dilution of the reaction solution. The formation

TABLE 3. Changes in $[\eta]$ and Molecular Weight Averages with PVC Concentration: Thermal Dehydrochlorination of PVC in Pyridine at 120°C for 135 min

PVC concentration (g/L)	Conversion x (%)	$[\eta]$ (dL/g)	\bar{M}_n	\bar{M}_w	H
41.7	3.62	0.81	37,900	109,300	2.8
31.3	3.82	0.78	28,700	100,600	3.5
28.0	4.34	0.76	26,100	83,700	3.2
25.0	5.10	0.75	18,900	70,100	3.6

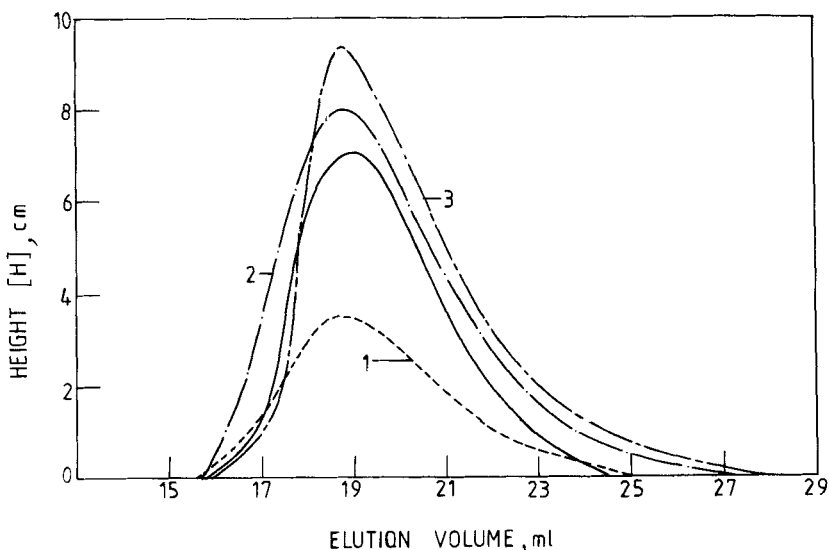


FIG. 3. Thermal dehydrochlorination of PVC in pyridine for 135 min at 120°C. Changes in MWD with PVC concentration of (1) 41.7, (2) 31.3, and (3) 28.0 g/L. (—) PVC.

of an increasing amount of low molecular weight material is perhaps the result of the predominance of chain scission reactions with dilution.

As the drop in \bar{M}_n was always higher compared to \bar{M}_w , H shows an increase.

In all the above cases the intrinsic viscosity changes did not follow the molecular weight changes closely. The reason may be because the

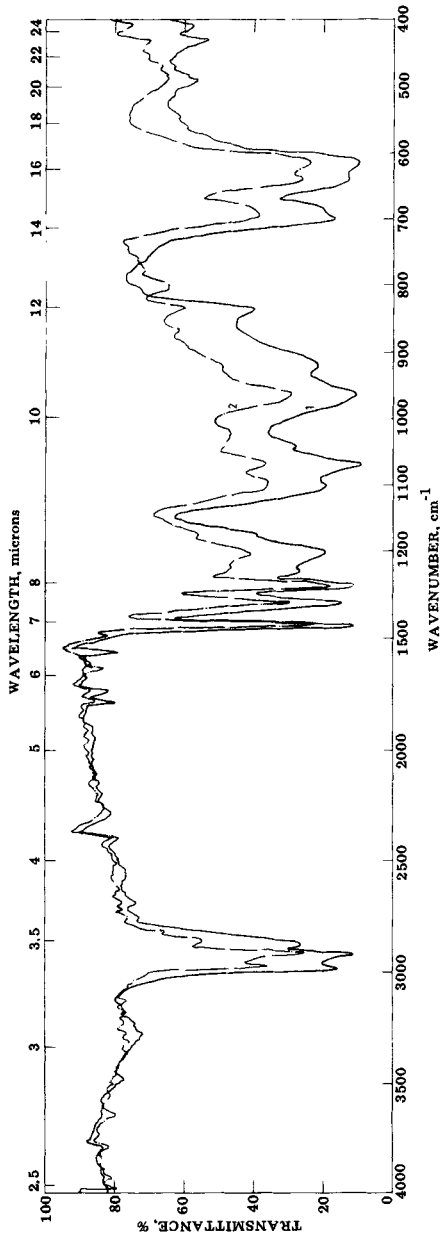


FIG. 4. Infrared absorption spectra of film cast from THF solution: (1) PVC and (2) PVC dehydrochlorinated for 180 min at 120°C in pyridine (41.7 g/L).

TABLE 4.

Assignments	Absorption bands (cm^{-1})
C-Cl stretching	615, 690
CH ₂ rocking	960
CH bending	1250, 1340
CH ₂ bending	1430
C=C stretching (due to internal unsaturation)	1610
C=O stretching (arising from some oxidation of PVC and traces of added substances such as stabilizers)	1740, 1780
Aliphatic C-H stretching	2930

accompanying chain scission reactions make partly successful the increase in molecular weight due to cross-linking by measuring $[\eta]$, of the polymer solution, as observed earlier by Bengough and Sharpe [10].

Characterization of Polyene Sequences

Infrared spectroscopy has been used to ascertain the presence of conjugated double bonds in DHPVC. By comparing the spectra of DHPVC with that of PVC (Fig. 4) it became evident that as far as the major peaks are concerned, they occur in the same position in DHPVC as in virgin PVC. The assignments of the main absorption peaks of PVC as well as of DHPVC are given in Table 4.

The assignments of the absorption bands of PVC and DHPVC have also been discussed in the literature [11].

Unlike the original PVC, however, the DHPVC also exhibited a band at 1635 cm^{-1} arising from the conjugated polyene sequences. The presence of conjugated double bonds in infrared spectra of DHPVC has been shown earlier by Shindo et al. [11].

To follow more closely the conjugated double bonds and their sequence distribution, ultraviolet spectroscopy has been used. In the absorption spectra of dehydrochlorinated PVC there will be several bands for each molecule having n conjugated double bonds. In DHPVC, n will have many values. Consequently, the spectrum of dehydrochlorinated PVC will be an integral of the spectra of various polyenes present in the dehydrochlorinated product. Therefore, it is very difficult to determine exactly the distribution of the values of n in

TABLE 5. Absorption Maxima for Different Lengths of Conjugated Double Bond Sequences

Number of conjugated double bonds (n)	λ (nm)		Lechermeier ^c	Our work	Molar absorption coefficient ϵ_{λ} (Daniels and Rees) ^b
	Abbas ^a	Daniels and Rees ^b			
2	-	-	235	238	20,000 ^d
3	288	240, 248, 257, 268	260-272	257	42,700
4	308	267, 278, 290, 304	305	288	78,600
5	324	279, 290, 303, 317, 334	322	325	121,000
6	340	300, 313, 328, 344, 364	355	340	138,000
7	364	316, 332, 350, 368, 390	360	358	177,100
8	388	332, 349, 367, 386, 410	385	-	210,000
9	412	345, 363, 380, 404, 430	408	-	242,800
10	434	358, 376, 397, 420, 447	430	-	275,600

^aData of Abbas and Sorvik [13].^bData of Daniels and Rees [12].^cData of Lechermeier, Revillon, and Pillot [14].^dAssumption.

TABLE 6. Variation in N , T_n , D_n , and P_n with Time of Dehydrochlorination: Thermal Dehydrochlorination of PVC in Pyridine (41.7 g/L) at 120°C

Dehydrochlorination time (min)	Conversion x (%)	Number, N , of polyenes having conjugated double bonds (n) of							T_n	D_n	P_n (%)
		2	3	4	5	6	7				
45	2.13	1.50	0.59	0.13	0.07	0.05	0.03	2.37	6.15	0.40	
90	3.42	1.52	0.67	0.17	0.07	0.06	0.04	2.53	6.73	0.45	
135	3.62	4.22	1.77	0.54	0.19	0.15	0.10	6.97	18.48	1.20	
180	4.53	7.95	3.26	0.98	0.38	0.32	0.23	13.13	35.08	2.28	

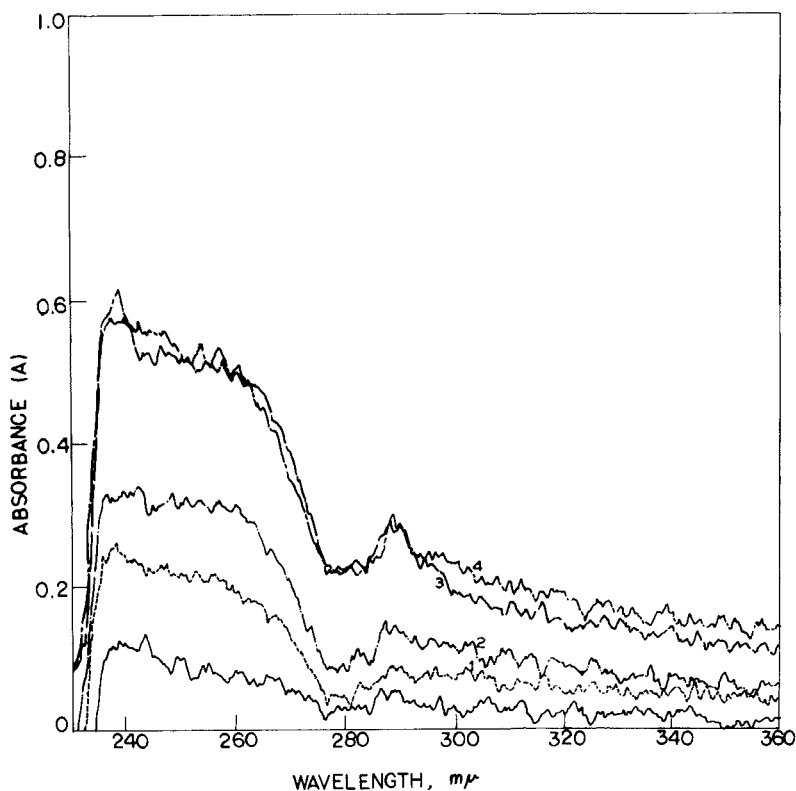


FIG. 5. Thermal dehydrochlorination of PVC in pyridine (41.7 g/L) at 120° C. Changes in ultraviolet absorption spectra with dehydrochlorination time of (1) 45, (2) 90, (3) 135, and (4) 180 min. (—) PVC.

DHPVC. We have used the work of Daniels [12], Abbas [13], and Lechermeier [14] for indexing the peaks. Table 5 gives the value of the absorption coefficients and the corresponding wavelengths of the peaks from the literature and from our study. These values enable us to calculate the individual concentrations of the different polyenes. The concentration of polyenes having n conjugated double bonds in DHPVC was calculated by using Beers law:

$$A_{\lambda} = \epsilon_{\lambda} C_n d$$

where d is the cell path length in cm, ϵ_{λ} is the absorption coefficient corresponding to n -th double bond in L/mol cm units, C_n is the

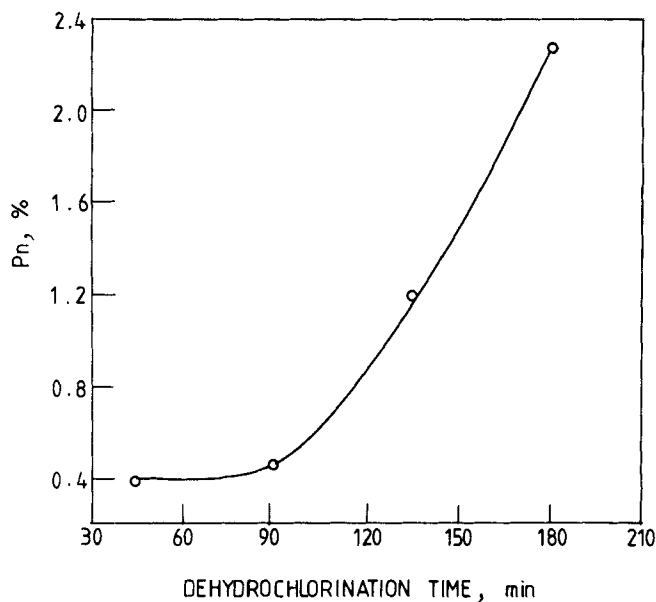


FIG. 6. Dependence of percentage of double bonds, P_n (%), upon the reaction time. Thermal dehydrochlorination of PVC in pyridine (41.7 g/L) at 120°C.

concentration of the n -th double bond in mol/L, and A_λ is the absorbance at the wavelength corresponding to n -th double bond absorption.

Dividing the polyene concentration C_n by the concentration of DHPVC (cell concentration in mol/L), we can obtain the number of polyenes, N , having n conjugated double bonds in the polymer. From the values of N , the total number of polyenes (T_n) and the number (D_n) and percentage (P_n) of double bonds in the dehydrochlorinated product can be calculated [15].

Changes in Polyene Sequence Length Distribution with Dehydrochlorination Time

Table 6 depicts that both the length of the polyene sequences and the total number of double bonds increases continuously (Figs. 5 and 6) with an increase in reaction time.

TABLE 7. Variation in N , T_n , D_n , and P_n with Temperature of Dehydrochlorination: Thermal Dehydrochlorination of PVC in Pyridine (41.7 g/L) for 135 min

Dehydrochlorination temperature (°C)	Conversion x (%)	Number, N , of polyenes having conjugated double bonds (n) of							T_n	D_n	P_n (%)
		2	3	4	5	6	7				
120	3.62	4.22	1.77	0.54	0.19	0.15	0.10	6.97	18.48	1.20	
125	3.82	5.00	2.27	0.64	0.30	0.23	0.17	8.61	23.44	1.52	
135	4.14	5.90	2.60	0.73	0.30	0.23	0.18	9.94	26.66	1.73	
150	5.63	3.68	1.55	0.47	0.19	0.16	0.11	6.17	16.60	1.08	

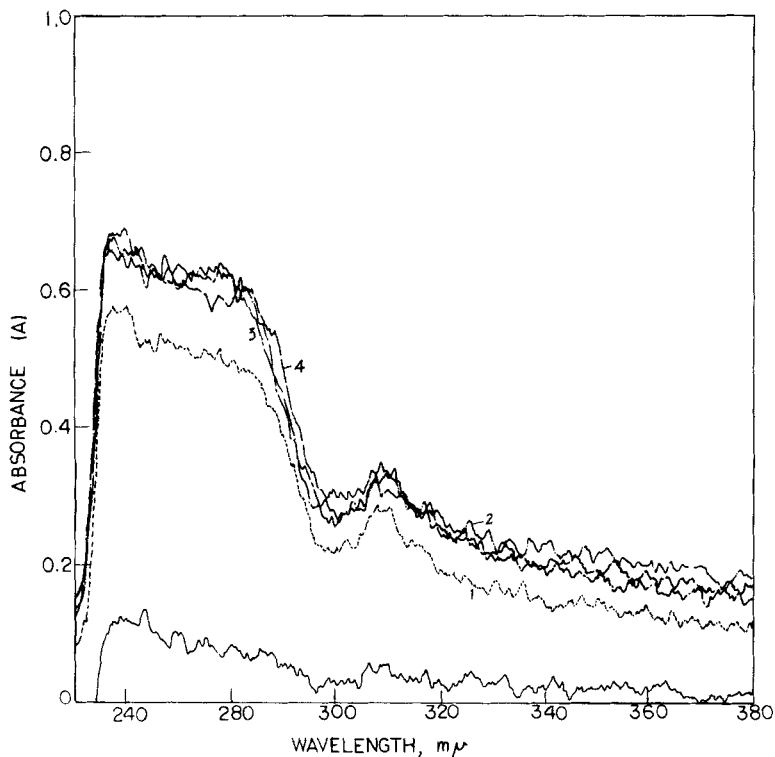


FIG. 7. Thermal dehydrochlorination of PVC in pyridine (41.7 g/L) for 135 min. Changes in ultraviolet absorption spectra with dehydrochlorination temperature of (1) 120, (2) 125, (3) 135, and (4) 150°C. (—) PVC.

Changes in Polyene Sequence Length Distribution with Dehydrochlorination Temperature

From the data in Table 7 an increase in the length of the polyene sequences with an increase in dehydrochlorination temperature is observed up to 125°C. A further increase in reaction temperature lowered the fraction of long polyene sequences, and thus the discoloration. The ultraviolet spectra of DHPVC prepared at 135 and 150°C showed the effect (Fig. 7). Table 7 also shows that with increase in the reaction temperature the total number of double bonds increased continuously up to 135°C, followed by a rapid decrease at 150°C (Fig. 8).

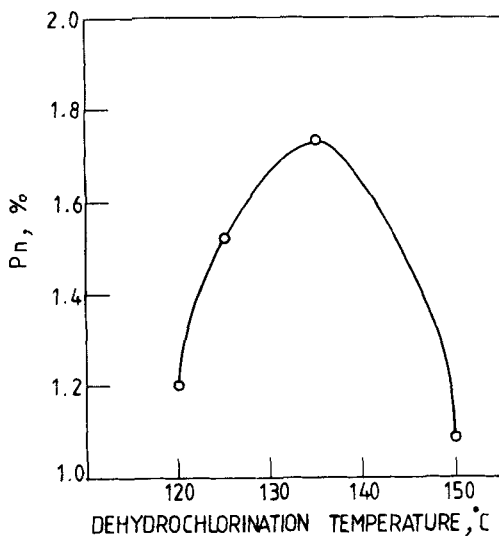


FIG. 8. Dependence of percentage of double bonds, P_n (%), upon the reaction temperature. Thermal dehydrochlorination of PVC in pyridine (41.7 g/L) for 135 min.

Changes in Polyene Sequence Length Distribution with Concentration

Table 8 shows that with a decrease in PVC concentration in the dehydrochlorination reaction, both the length of the polyene sequences and the total number of double bonds decreases continuously (Figs. 9 and 10). This can be attributed to the increase in chain scission reactions with dilution (Table 3).

It was observed, in general, that the shorter polyenes were maximum and their concentration decreased continuously with an increase in their length.

DISCUSSION

For the thermal dehydrochlorination of PVC in pyridine, an ionic molecular elimination mechanism involving an intermediate complex (I) formation, due to solvent-polymer interaction, has been proposed in our earlier studies [8].

Our present results show that an increase in dehydrochlorination time is followed by an increase in the total number of double bonds as well as in the polyene sequence lengths. Cross-linking also

TABLE 8. Variation in N , T_n , D_n and P_n with PVC Concentration: Thermal Dehydrochlorination of PVC in Pyridine at 120°C for 135 min

PVC concentration (g/L)	Conversion x (%)	Number, N, of polyenes having conjugated double bonds (n) of							T_n	D_n	P_n (%)
		2	3	4	5	6	7				
41.7	3.62	4.22	1.77	0.54	0.19	0.15	0.10	6.97	18.48	1.20	
31.3	3.82	3.37	1.53	0.39	0.17	0.12	0.09	5.68	15.14	0.98	
28.0	4.34	3.00	1.40	0.36	0.16	0.12	0.08	5.12	13.72	0.89	
25.0	5.10	3.00	1.18	0.42	0.16	0.12	0.09	5.02	13.50	0.87	

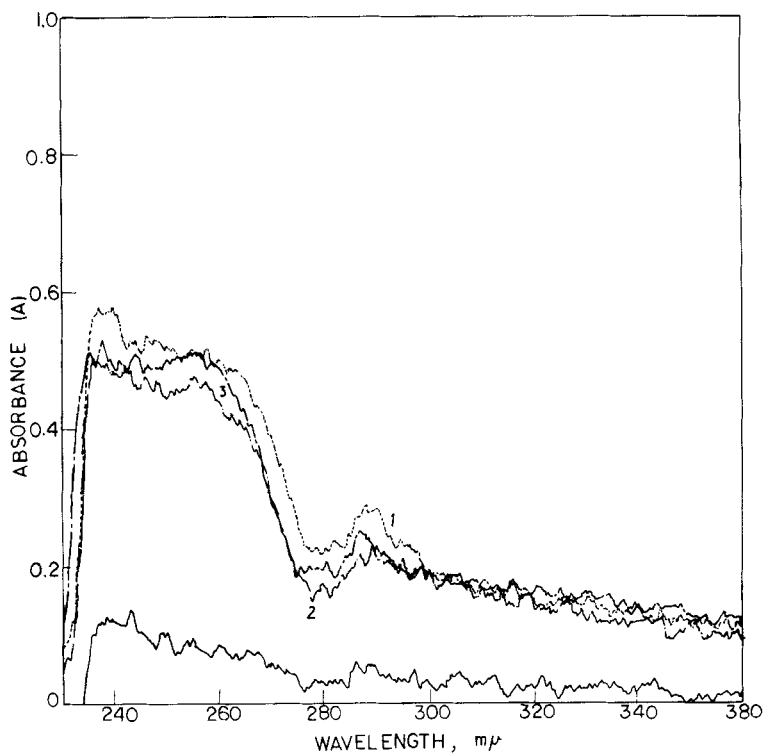


FIG. 9. Thermal dehydrochlorination of PVC in pyridine at 120°C for 135 min. Changes in ultraviolet absorption spectra with PVC concentration of (1) 41.7, (2) 31.3, and (3) 28.0 g/L. (—) PVC.

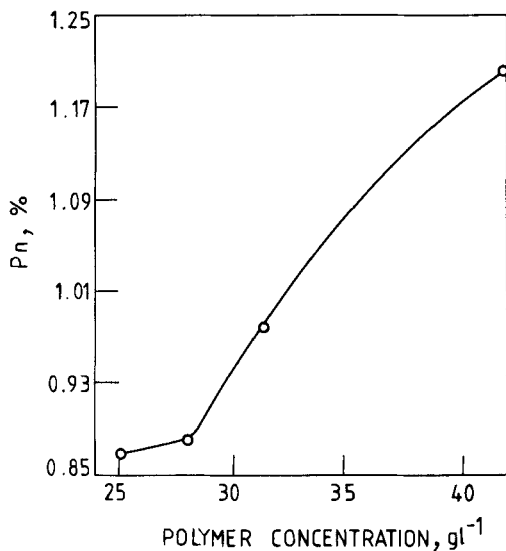
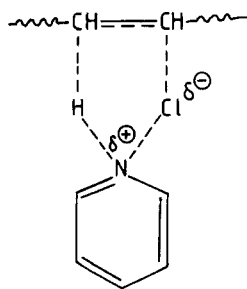


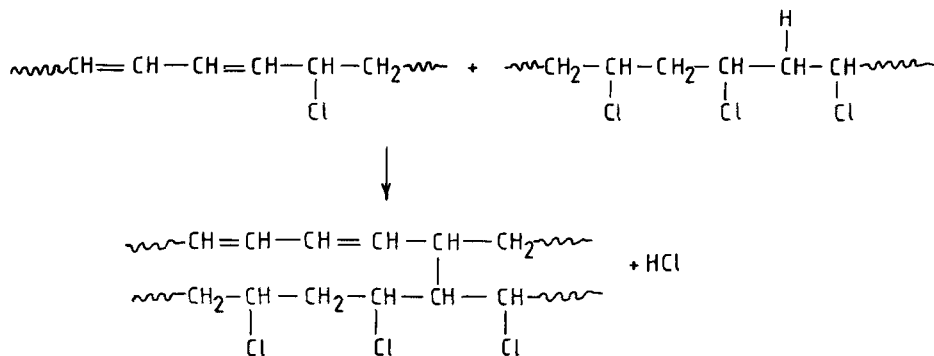
FIG. 10. Dependence of percentage of double bonds, P_n (%), upon PVC concentration. Thermal dehydrochlorination of PVC in pyridine at 120°C for 135 min.



(I)

increases continuously. Higher cross-linking with longer polyenes can only be explained by the intermolecular interaction of long conjugated double bond sequences. A similar effect was observed by Bengough and Sharpe [10] who showed that after a sufficiently long time of dehydrochlorination even short polyene sequences may undergo secondary reactions, although these reactions were favored by longer polyenes. An increase in dehydrochlorination temperature results in

a less pronounced discoloration (Table 7) and increased cross-linking (Table 2). The connection between higher cross-linking and lower discoloration at higher temperatures is explained by the fact that at higher reaction temperature a cross-linking reaction competes with the polyene propagation. A cross-dehydrochlorination mechanism (intermolecular elimination of HCl) as suggested by Druessedow and Gibbs [6] is in accordance with such a behavior:



Extensive cross-linking results in some insolubility [8] of the product. These results are consistent with those obtained by Abbas and Sorvik [16] in the thermal degradation of PVC in nitrogen atmosphere.

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