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Investigation of Thermal Degradation of PVC in the Solid State

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ABSTRACT

The thermal degradation of PVC powders and the inhibition of this process by cadmium laurate was investigated by the measurement of discoloration, diffuse reflectance spectra, and the quantity of hydrochloric acid formed. Kinetic analysis of the data obtained by us previously showed that both the data of color measurements and those of diffuse reflectance spectra may be used conveniently for the calculation of the number of double bonds formed during the degradation.

INTRODUCTION

Little attention has been paid, so far, to the diffuse reflectance spectra of powdered samples in the investigation of PVC degradation, although, this method has many advantages in comparison with measurements in solution [1]. The results can be readily correlated with the discoloration of PVC; therefore, this technique was applied in our experiments, too.

Our previous study [2] showed that the discoloration of PVC can be best measured by means of the "brightness factor", which is the Y coordinate of the CIE color measuring system. We have found the following correlation to hold between the discoloration and the amount of hydrochloric acid, HCl, liberated during the dehydrochlorination (which is practically in correspondence with the number of double, bonds, n, formed):

$$\mathrm{HCl} \approx n = (w/\alpha_Y)(1 - R_Y)t \qquad (1)$$

where $R_Y = Y/100$, w is the rate of initiation, α_Y is a proportionality factor, and t is time.

The correctness of this correlation has been further checked by measuring of the discoloration with the aid of diffuse reflectance spectra.

The applicability of Eq. (1) for the determination of double-bond formation was illustrated by detailed kinetic study of inhibiting action of cadmium laurate on the dehydrochlorination process.

DISCOLORATION AND DIFFUSE REFLECTANCE SPECTRA

Samples of PVC powders and their combination with 2.5% cadmium laurate (CdL_2) were degraded in an N_2 atmosphere at 165°C. The course of degradation was followed by the simultaneous measurement of R_Y and hydrochloric acid liberation, and also by the measurement of diffuse reflectance.

The result of these measurements are shown in Fig. 1, where the amount of HCl is plotted against $(1 - R_Y)t$. According to this, the validity of Eq. (1) becomes apparent.

From a knowledge of the slopes of the straight lines w/α_Y, values of n or HCl can be calculated at any optional point of time. This is especially useful in calculations relating to the induction period, when samples stabilized with HCl acceptors are used.

On extending Eq. (1) for diffuse reflectance spectral measurements, we have to consider that Y was determined in a special instrument equipped with the color filter specified by the CIE system. Using this color filter we obtain a percentage value of the weighted average of

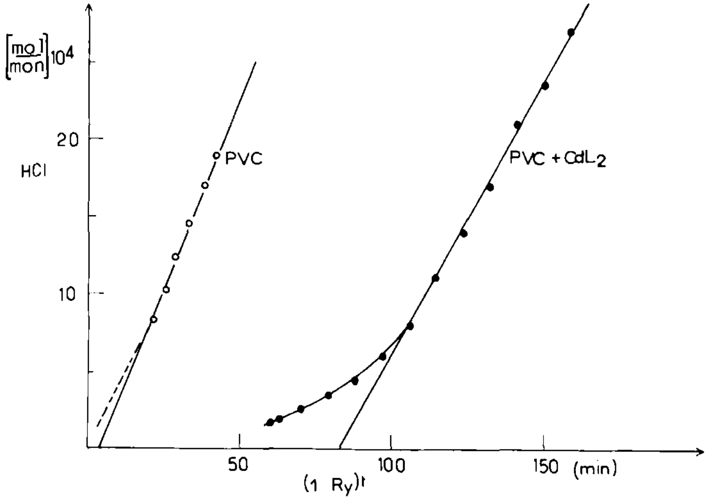

FIG. 1. Graphical representation of Eq. (1) in linearized form.

the quantity of light reflected in this wavelength region (λ = 380-770 nm). It was, therefore, necessary to investigate whether each single reflectance value R_i, which can be ordered to a certain polyenic sequence, also follows Eq. (1) (where i = 2, 3, etc., denotes the number of conjugated double bonds in the polyene sequence).

For this reason, Eq. (1) was transformed as follows:

$$n_i = (w/\alpha_i)(1 - R_i)t \tag{2}$$

where n_i is the total number of double bonds in the polyene sequences with conjugation number i.

Since n_i cannot be calculated directly from the spectral data (Fig. 2), we determined the k/s value which is proportional to it and can be obtained from the Kubelka-Munk equation, commonly used in the evaluation of reflectance spectra. According to this:

$$k/s = (1 - R_i)^2/2R_i = (\epsilon/s)n_i \tag{3}$$

where k is the absorption coefficient and ϵ/s is the quotient of the coefficients of the specific absorption and scattering.

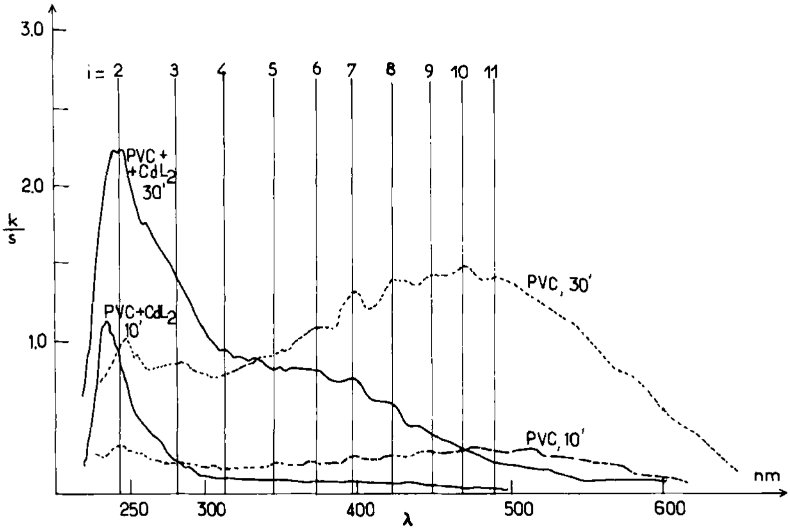

FIG. 2. Diffuse reflectance spectra of PVC powder and its combination with 2.5% cadmium laurate after degradation for 10 and 30 min.

Plots of $(\epsilon/s) \sum_{2}^{11} n_i$ versus $(1 - \overline{R}_i)t$ are straight lines in a fairly good approximation ($i = 2$ to 11, $\overline{R}_i$ is the arithmetic mean of the reflectance values, R_i). The slopes of the lines are $[(\epsilon/s)\cdot(w/\overline{\alpha}_i)]$, as it follows from Eq. (4):

$$(\epsilon/s) \sum_{2}^{11} n_i = (\epsilon/s)(w/\overline{\alpha}_i)(1 - \overline{R}_i)t \qquad (4)$$

which is analogous to Eq. (1). This analogy can be seen in Fig. 3, and from the data of Table 1, in which the rates of dehydrochlorination v_{HCl} and the slopes of the lines w/α_Y and $(\epsilon/s)(w/\overline{\alpha}_i)$ are listed.

The (ϵ/s) w values in Table 1 were calculated from the $(\epsilon/s)n_i$ values of the diffuse reflectance spectra, assuming the rate of initiation w to be constant, i.e., $z = wt$, where z is the number of the polyene sequences. In Table 1, k_2 and k_1 are the rate constants of the chain propagation and termination, respectively.

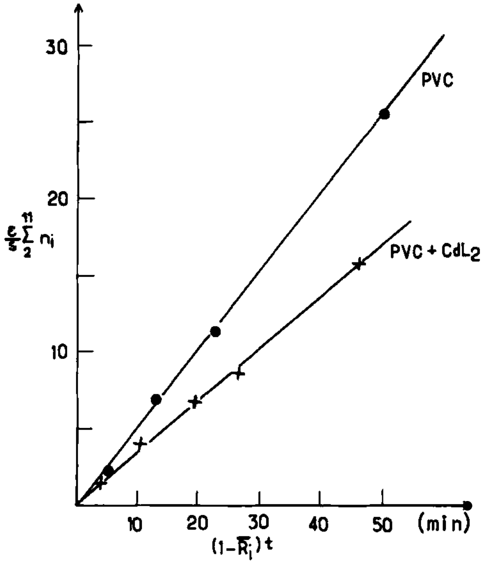

FIG. 3. Graphical representation of Eq. (2) in linearized form.

TABLE 1.

	Dehydrochlorination $v_{HCl} = w(k_2/k_1)$ (mole/mon-min)	Discoloration (system R_Y) w/α_Y (mole/mon-min)	Reflectance spectrum (system R_i)		
			$\frac{\epsilon w}{s\bar{\alpha}_i}$ (min^{-1})	$(\epsilon/s)\, w$ (min^{-1})	$\bar{\alpha}_i$
PVC	0.43×10^{-4}	0.50×10^{-4}	0.52	0.078	0.150
PVC + CdL$_2$	0.34×10^{-4}	0.36×10^{-4}	0.35	0.073	0.208

As $z = \sum_{1}^{\infty} n_i/i$, the data of the reflectance spectrum lead to the relation:

$$(\epsilon/s)z \approx (\epsilon/s) \sum_{2}^{11} n_i/i$$

$$\approx (\epsilon/s)\, wt \qquad (5)$$

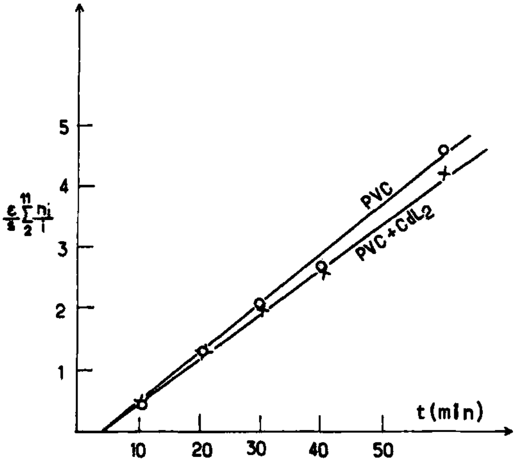

FIG. 4. Time dependence of polyene formation.

(where sequences with i = 1 and i > 11 are not considered, as they could not be identified in the spectra). Equation (5) is graphically shown, as $(\epsilon/s)\ \sum_{2}^{11} n_i/i$ vs. t, in Fig. 4. The nearly identical slopes of the lines in Fig. 4 indicate that the rate of initiation practically is not affected by the addition of CdL_2. The data relating to system R_i in Table 1 allow the calculation of $\bar{\alpha}_i$. Supposing that $\alpha_Y \sim \bar{\alpha}_i$, the approximate values of k_2/k_1 and w can also be calculated; these are shown in Table 2.

The values obtained for PVC are in agreement with data published elsewhere [3, 4]. The presence of CdL_2 and of the $CdCl_2$ formed from it results in the decrease of the k_2/k_1 values, which is probably due to a higher rate of the chain termination reaction.

In the calculations described above, no consideration was given to the presumable effect of charge-transfer complexes (formed by the addition of cadmium laurate or $CdCl_2$ to the double bonds) on the spectra of the pure polyenes. According to our further investigations, not yet published, the presence of such complexes gives rise to only slight differences; thus the validity of Eqs. (4) and (5) and the data in Tables 1 and 2 remain essentially unchanged.

TABLE 2.

	w (mole/mon-min)	k_2/k_1
PVC	0.075×10^{-4}	5.7
PVC + CdL_2	0.075×10^{-4}	4.5

KINETICS OF THE INHIBITING ACTION OF CADMIUM LAURATE

The inhibiting action of CdL_2 was investigated by considering the change in the double bond formation caused by the action of CdL_2. The amount of double bonds was calculated from the R_Y data by means of Eq. (1), by using the corresponding value of w/α_Y given in Table 1.

In order to obtain an equation which describes the time dependence of double bond formation, rate equations were derived, based on the well-known mechanism for the stabilizing action of metallic soaps [5-9]. We assumed that in the presence of CdL_2 some of the allyl-activated chlorine atoms are replaced by ester groups. This reaction increases the rate of chain termination in the dehydrochlorination process. The ester groups produced, however, gradually undergo acidolysis, regenerating the allyl-activated chlorine; this results in the subsequent increase of the rate of chain propagation.

This mechanism can be expressed by rate equations for the single steps of the dehydrochlorination process, as follows:

$$dz^*/dt = w - \underbrace{k_1z^* - k_3z^*x}_{\text{chain termination}} + \underset{\text{regeneration by acidolysis}}{k_4y} \tag{6}$$

$$dy/dt = \underset{\text{ester formation}}{k_3z^*x} - \underset{\text{acidolysis by HCl}}{k_4y} \tag{7}$$

$$dx/dt = -k_3z^*x - \underbrace{[(dn/dt) - (dHCl/dt) - k_4y]}_{CdCl_2 \text{ formation}} \tag{8}$$

$$dn/dt = k_2z^* \tag{9}$$

where z^* is the concentration of allyl-activated polyenes, x is the concentration of CdL_2, y denotes the concentration of ester groups, n is the concentration of double bonds; HCl represents the amount of hydrogen chloride liberated. K_1, k_2, k_3, and k_4 are the rate constants of chain termination, propagation, esterification, and acidolysis, respectively.

When expressing dn/dt from Eqs. (6), (7), and (9), and taking the steady-state condition, $dz^*/dt = 0$, after integration we get Eq. for the formation of double bonds:

$$n = w(k_2/k_1)t - (k_2/k_1)y \qquad (10)$$

The summation of Eqs. (7) and (8), and subsequent integration leads to the material balance equation of CdL_2:

$$x_0 = (n - HCl) + y + x \qquad (11)$$

where x_0 is the initial concentration of CdL_2.

In Fig. 5 the number of double bonds is plotted as a function of time. The double bond formation, according to Eq. (10), is initially very slow, due to the inhibiting action of the ester group formation. At the time of appearance of hydrogen chloride (after approximately

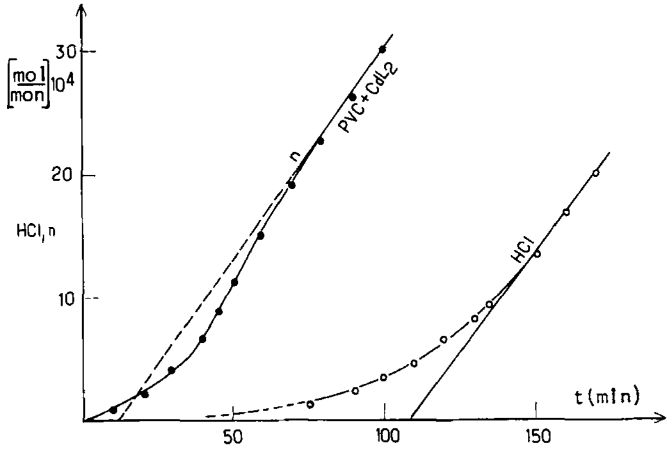

FIG. 5. Inhibiting action of cadmium laurate on the formation of double bonds and hydrochloric acid.

40 min) the sample already contains a rather high amount of accumulated and dissolved HCl. Therefore, as shown by the curve, acidolysis takes place with the consequent rapid increase of the rate of double bond formation. Finally, when the ester groups have been removed, the curve becomes linear, which is characteristic of the stationary phase.

The curve also permits the calculation of the amount of ester groups formed, since, as evidenced by Eq. (10), the difference between the curve and the line extrapolated from the linear section equals $(k_2/k_1)y$.

Figure 6 compares the values of y calculated in this manner as a function of time with those obtained on the basis of the diffuse reflectance spectra. Rather good agreement can be observed. Values of y from the diffuse reflectance spectra were obtained by calculating the approximate average polyene lengths

$$K = \sum_{2}^{16} (\epsilon/s)n_i / \sum_{2}^{16} (\epsilon/s)z_i$$

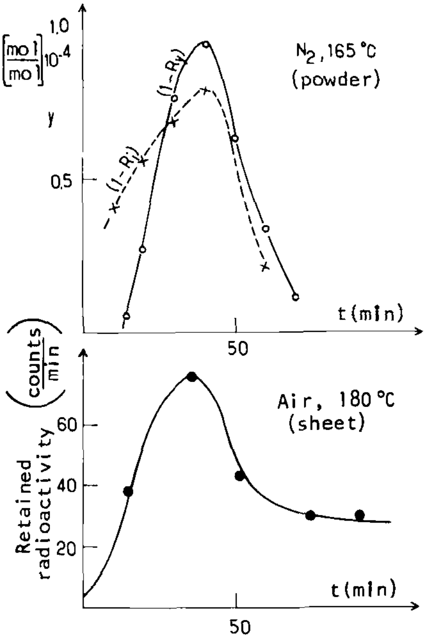

FIG. 6. Time dependence of the formation of ester groups.

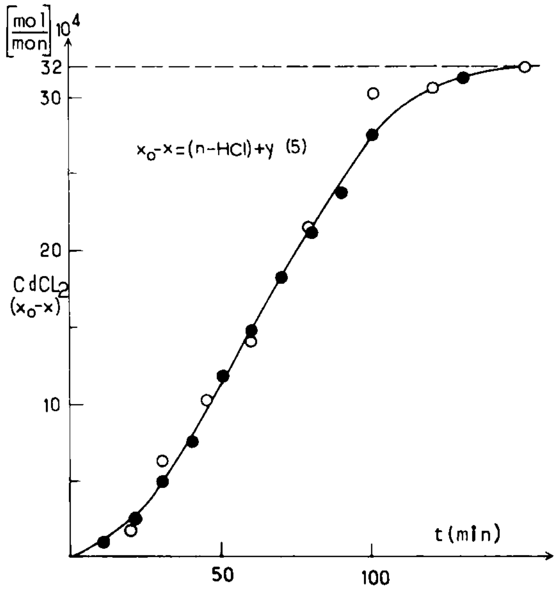

FIG. 7. Comparison of calculated concentration values of $CdCl_2$ with those obtained by infrared measurements: (○) from infrared spectra; (●) $(1 - R_y)$ system.

The wavelengths λ_i for higher length (i = 12 - 16) were determined by extrapolation, using the well-known equation, $\lambda_i = a + b\sqrt{i}$, found to be valid for i = 2 - 11.

On the other hand, $\overline{K} = n/z = n/wt$. On substituting n from Eq. (10) into this latter equation and solving for y we obtain:

$$y = w\ \{1 - [\overline{K}/(k_2/k_1)]\}t$$

Values for w and k_2/k_1 were taken from Table 2.

The lower graph in Fig. 6 illustrates the measurements by Frye and Horst [5] using the radioactive tracer method.

It is remarkable that the maximum amount of the ester formed is very small (about 1×10^{-4} mole for one monomeric unit), which corresponds to about 3% of the amount of the stabilizer used.

The consumption of the stabilizer, i.e., the $CdCl_2$ formation can be calculated from the material balance equation from a knowledge of y and n. Figure 7 shows that the resulting data are in good agreement with those obtained by our infrared carboxylate determinations on solid powders. The IR determination was carried out at 6.55 μ; each sample contained 20 mg of PVC powder and 1 g KBr in disc form.)

REFERENCES

[1] A. Guyot and M. Bert, J. Appl. Polym. Sci., 17, 753 (1973).
[2] G. Ocskay, J. Lévai, Zs. Nyitrai, E. Szabados, and F. Várfalvi, Eur. Polym. J., 10, 1121 (1974).
[3] K. S. Minsker, D. V. Kazachenko, R. G. Abdullina, R. B. Kovler, and A. A. Berlin, Vysokomol. Soedin., A 15, 866 (1973).
[4] G. Ocskay and G. Lévai, paper presented at the International Symposium on Macromolecules, Madrid, 1974; Preprints 1, 478 (1974).
[5] A. H. Frye and R. W. Horst, J. Polym. Sci., 40, 417 (1959).
[6] W. I. Bengough and M. Onozuka, Polymer, 6, 625 (1965).
[7] T. V. Hoang, A. Michel, and A. Guyot, Eur. Polym. J., 12, 337 (1976).
[8] D. F. Anderson and D. A. McKenzie, J. Polym. Sci. A-1, 8, 2905 (1970).
[9] A. H. Frye and R. W. Horst, J. Polym. Sci., 45, 1 (1960).

DISCUSSION

Dr. Abeler (Ciba-Geigy, West Germany): Dr. Ocskay showed that there is a correlation between the CIE value, Y, and the HCl evolution. Unfortunately, in the early stage of discoloration, the changes in Y are so small that they cannot be used to describe the so-called early color. We usually take the yellowness index–I expect that he knows that index–and it is also possible to take the changes of the z value, as was shown by Tielerdt in Darmstadt [Angew. Makromol. Chem., 47, 129 (1975)]. Did Dr. Ocskay find similar correlation between these coordinates and HCl evolution?

Dr. Ocskay: First, I should like to say that I read Dr. Abeler's recent article [Kunststoffe, 66, 369 (1976)]. We are aware of the fact that for the exact determination of a degree of discoloration several other factors must be considered, that is, other measurements are also needed. In practice, however, as mentioned in Dr. Abeler's paper, simple measurement of the Y coordinate gives fair or good results, which we have also found satisfactory in the early stage of discoloration. These results may not exactly define the color, yet they can be used for calculation of e. g., the amount of HCl liberated; thus in the presence of stabilizers, we need to apply the much more troublesome analytical methods.