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Initial Steps in Thermal Degradation of Fractions of PVC with Different Tacticities

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ABSTRACT

PVC samples were prepared in bulk by using AIBN and UV radiation as the initiator system. The polymerization temperatures were 40, 0, -25, and -50°C. The samples were fractionated by means of successive extractions with dioxane, tetrahydrofuran, and cyclohexanone, and two fractions of each sample were characterized in order to study their thermal degradation. This was carried out by conductivity measurements with the use of a differential conductimetry cell for degradations up to 0.1% and a single cell for degradations up to 0.4%. From the UV-visible spectra of equally degraded samples it is concluded that the higher the tacticity of PVC, the higher the proportion of long polyene sequences is; this behavior is independent of the

conversion. The degraded samples were ozonized in order to measure the number of scissions per chain. This number was found to be low for syndiotactic samples and high for atactic samples, which is accounted for by the increased clustering of double bonds to form long polyene sequences in the more syndiotactic polymers. Previous results suggesting increased ease of propagation along syndiotactic sequences are therefore confirmed more quantitatively.

INTRODUCTION

Although many publications during recent years have dealt with the degradation of PVC, the possible influence of the tacticity on mechanism of degradation was not taken into consideration. However, in some recent papers we showed the propagation step to depend on the content of syndiotactic polymer [1-4]. The degradation rate appeared to be higher, the greater the content of syndiotactic sequences; such behavior was thought to be due to the increased ease of propagation along syndiotactic sequences in comparison with that along atactic parts.

In spite of these striking results, some doubt arose from the fact that polymers were either unfractionated [1-3] or showed differences in properties which might give rise to confusion.

We have now studied the thermal degradation of well known fractions with definite tacticity [5] and compared the results for the very initial steps (about 0.1%) by means of a differential conductimetry cell [6] with those obtained for conversions up to 0.4% using a single conductimetry cell [3]. Satisfactory correlation between the two methods was previously found [2].

In order to verify the polyene sequence distribution in degraded samples as given by ultraviolet-visible spectroscopy, we determined the average number of chain scissions by means of ozonolysis and the osmometrically determined molecular weights.

EXPERIMENTAL

Polymer Preparation and Fractionation

Samples of PVC were prepared as described previously [2, 3] in bulk by using AIBN and ultraviolet radiation as initiator system, so allowing the use of low temperatures without changing the remaining experimental conditions in order to obtain differences in tacticity.

The temperatures used were: 40°C (samples A); 0°C (for sample B); -25°C (for sample C) and -50°C (sample D).

Taking into account previous results on fractionation of PVC from the point of view of tacticity [5], the samples were fractionated by means of successive extractions with dioxane (fraction 1), tetrahydrofuran (fraction 2), at 25°C and cyclohexanone at 50 (fraction 3) and 120°C (fraction 4). The extractions were carried out in a magnetically stirred vessel set in a thermostat for 24 hr. After recovery of the undissolved material each fraction was precipitated with methanol, washed several times, and dried under vacuum at 40°C. Among all the obtained fractions we chose the two most significant from the point of view of either the available weight or the tacticity content (Table 1).

Characterization of Fractions and Degraded Samples

The samples were characterized by determining the intrinsic viscosity in cyclohexanone at 30°C, the IR absorbance ratio A_{1428}/A_{1434} as a relative measure of the syndiotactic sequence content [7], \bar{M}_w and \bar{M}_n by GPC, and the number-average molecular weight by osmometry. The osmometric experiments were carried out in a Hewlett-Packard 502 high-speed membrane osmometer using solutions in purified cyclohexanone. Care was taken to heat the solutions at 110°C for 1 hr before making measurements at 30°C (Table 1).

To determine \bar{M}_w and \bar{M}_n by GPC, a Waters apparatus was used under the following conditions: solvent, hexamethylenephosphortriamide; temperature, 103°C; sample concentration, 0.5%; flow rate, 1.5 ml/min. The column calibration was performed by using polystyrene samples from Waters (Table 1).

Dehydrochlorination Reaction

The degradation of samples was followed by measuring continuously the conductivity of the aqueous solution of HCl evolved. Two sets of experiments were carried out: for the first, a very sensitive differential conductimetry cell which is able to detect very low conversions was used, while a single cell was used in the second. Conversions of 0.1% and temperatures of 150 and 180°C were chosen for the first series, and conversions of 0.2, 0.3, and 0.4% were reached in the second series at 180°C. Further details have already been published [1, 3, 6].

TABLE I. Characteristics of Fractions

Sample	Solvent	A_{1428}		$[\eta]$ (ml/g)	\bar{M}_n (Osm)	\bar{M}_n (GPC)	\bar{M}_w (GPC)
		A_{1434}					
A1	Dioxane	1.12		92	47,500	37,500	101,000
A2	THF	1.17		-	-	86,000	172,000
B3	Cyclohexanone, 50°C	1.25		228	172,500	115,000	360,000
B4	Cyclohexanone, 120°C	1.25		-	-	92,500	288,000
C2	THF	1.33		-	-	37,500	132,000
C4	Cyclohexanone, 120°C	1.38		292	139,000	107,000	368,000
D2	THF	1.43		-	-	15,500	40,000
D4	Cyclohexanone, 120°C	1.56		216	76,200	78,000	286,000

TABLE 2. Ozonization Data for Samples Degraded to 0.1% (First Run)

Sample	$M_0 \times 10^{-3}$	$M \times 10^{-3}$	$(M_0/M) - 1$
A1 ^a	37.5	24.5	0.53
B3	115.0	54.0	1.13
C4	107.0	42.0	1.54
D4	78.0	41.0	0.90

^aDegraded only to 0.06%.

Ultraviolet-Visible Spectra

UV-Vis spectra were recorded on about 7% solutions in HMPT in a Cary 14 spectrometer. The solutions were carefully prepared under inert atmosphere at 40°C by using twice freshly distilled HMPT.

Ozonization Reactions

Samples degraded up to about 0.1% were ozonized under the following experimental conditions: 400 mg of degraded polymer were swollen in 150 ml of tetrachloroethane at 80°C for 2 hr. After cooling at -20°C, ozone was bubbled for 1.5 hr (samples A) or 3 hr (samples B, C, and D). Samples were then precipitated with methanol, filtered, and dried under vacuum at 40°C. The number-average molecular weight or ozonized samples was determined by GPC as above described. Table 2 summarizes the results obtained.

A second run of ozonizations was carried out for all the degraded samples, both those degraded to 0.1% and those degraded to 0.3%. Reactions were carried out with the use of chloroform and a small amount of methanol to swell the polymers as detailed by Geddes [8]. In order to ensure a complete reaction we extended the reaction time to 28 hr. The reaction temperature was 10°C, at which it was previously found that side reactions were minimal [9]. The ozonized polymers were precipitated with methanol and then filtered and dried under vacuum at 40°C. The number-average molecular weight of the ozonized samples was determined by osmometry as above described. The average number of scissions per chain was calculated by the equation

$$\bar{n} = (M_0/M) - 1$$

TABLE 3. Ozonization Data for Samples Degraded to 0.1% (Second Run)

Sample	$M_0 \times 10^{-3}$	$M \times 10^{-3}$	$(M_0/M) - 1$
A1 ^a	47.5	36.7	0.29
B3	172.5	37.7	3.57
C4	139.0	48.4	1.87
D4 ^b	76.2	56.5	0.34
D4	76.2	52.2	0.45

^aDegraded only up to 0.06%.

^bOzonization time: 11 hr.

TABLE 4. Ozonization Data for Samples Degraded to 0.3%

Sample	$M_0 \times 10^{-3}$	$M \times 10^{-3}$	$(M_0/M) - 1$
A1	47.5	18.2	1.61
B3	172.5	35.6	3.85
C4	139.0	-	-
D4	76.2	51.2	0.48

where M_0 and M are the number-average molecular weights of initial and ozonized polymer, respectively. The results are shown in Tables 3 and 4.

RESULTS AND DISCUSSION

Extractions with solvents of increasing polarity gives rise to fractions with increasing content of syndiotactic diads [5]. Nevertheless, apart from the small fractions which are overlooked here, the tacticity of fractions of each polymer lies in a well defined range which is related to the temperature of polymerization. According to previous results [3] there is a syndiotacticity range (about 1.13-1.20 for the ratio $A_{1428 \text{ cm}^{-1}}/A_{1434 \text{ cm}^{-1}}$) which corresponds to the most stable PVC. Moreover, this type of polymer was found to have a Bernoullian distribution of dyads in contrast with polymers having

an overall syndiotacticity content lower or higher than that of the quoted range; in both cases deviations from Bernoulli's statistics were observed, and these deviations appeared to be more marked, the higher the syndiotactic dyad content [7]. As shown in Table 1, fractions A and B lie in the above quoted range of tacticity and samples C and D, particularly the latter, are markedly syndiotactic. This seems to disagree somewhat with previous results [2], where unfractionated PVC prepared at 40°C was not thought to behave as a Bernoullian polymer. However, we found now that polymer A contains a 5% fraction of low syndiotacticity content which might account for the above results [2]. This conclusion supports that of Carman et al. [10], who found the deviations from Bernoulli's statistics to occur at polymerization temperatures higher than 40°C. The occurrence of three kinds of PVC from the point of view of tacticity is clearly stated.

The isotherms of degradation at low conversion (Fig. 1) clearly show the polymers to be more stable, the lower is the syndiotacticity content. To conversions up to 0.4% the isotherms are straight lines, their slopes are therefore the degradation rates (Table 5). Here again the higher the syndiotacticity content is, the higher the degradation rate, the most stable fractions being those where syndiotacticity content lies into the quoted range of Bernoullian distribution. These results confirm those obtained so far with unfractionated polymers [2-4].

The above differences in thermal degradation of PVC samples had been believed to be due to an increased ease of propagation along syndiotactic sequences [3]. Indeed, in these studies we found through UV-visible spectroscopy that the proportion of long polyene sequences in degraded polymers was greater, the higher the syndiotacticity content; similar results were recently obtained with copolymers of vinyl chloride with diethyl fumarate, isobutylene, and vinyl bromide

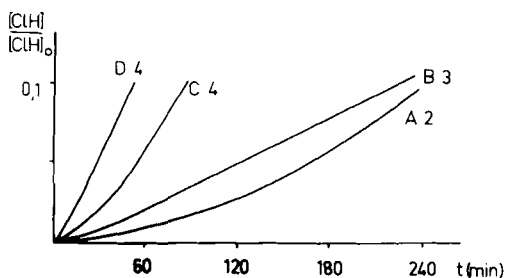


FIG. 1. Isotherms of degradation at 150°C (about 0.1%).

TABLE 5. Degradation Rates at 180°C to 0.3%

Sample	Degradation rate $\times 10^3$ ($[\text{HCl}]/[\text{HCl}]_0$)/min
A1	4.26
A2	4.85
B3	5.50
B4	5.88
C2	14.81
C4	14.78
D3	36.00
D4	29.20

having different syndiotacticity content in their PVC sequences [11]. Nevertheless, the fact that these studies dealt only with unfractionated polymers made it very interesting to consider more narrow fractions to assess the influence of tacticity on thermal degradation.

The results are shown in Figs. 2-7. Absorptions at wavelengths higher than 400 nm increase with increasing syndiotacticity content, which in principle involves an easier propagation along syndiotactic sequences. This might be explained by considering the propagation rate of polyene sequences along TT syndiotactic conformations to be higher than the termination rate, while the opposite is to be expected for atactic sequences, where TG conformations make it difficult for the trans-polyene sequences to occur.

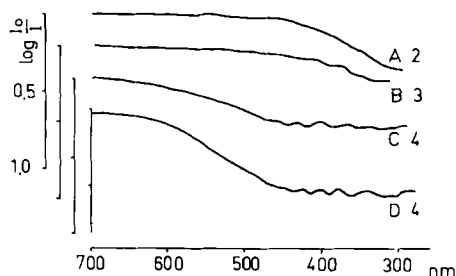


FIG. 2. UV-VIS spectra of degraded samples; 150°C (0.1%).

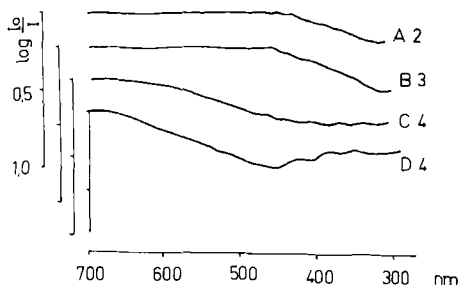


FIG. 3. UV-VIS spectra of degraded samples; 180°C (0.3%).

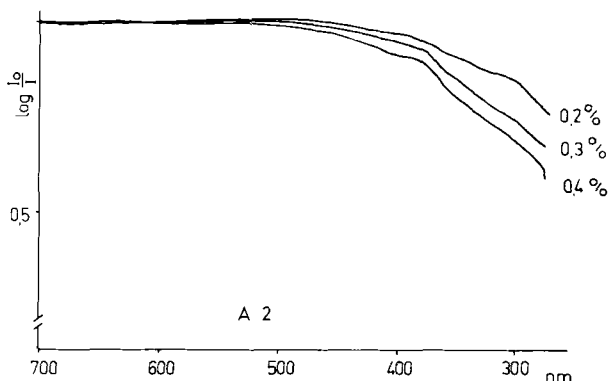


FIG. 4. Change in UV-VIS spectra vs. conversion (fraction A2).

On the other hand the evolution with increasing conversion of UV-visible spectra for each sample does not give rise to any change in their shape (Figs. 4-7), which leads us to consider the shape to be related only to the syndiotacticity content. Small though the number of syndiotactic sequences is, it should be sufficient to result in an increase of absorption at high wavelengths on account of the high extinction coefficient of long polyene sequences [12]. The behavior in the non-syndiotactic parts must be similar to that of atactic polymers, which may explain the fact that apart from absorptions at wavelengths higher than 400 nm in syndiotactic samples, the region 300-400 nm in UV-visible spectra is very similar for all the samples.

The shape of the UV-visible spectra accounts only qualitatively for the influence of the tacticity on thermal degradation of PVC.

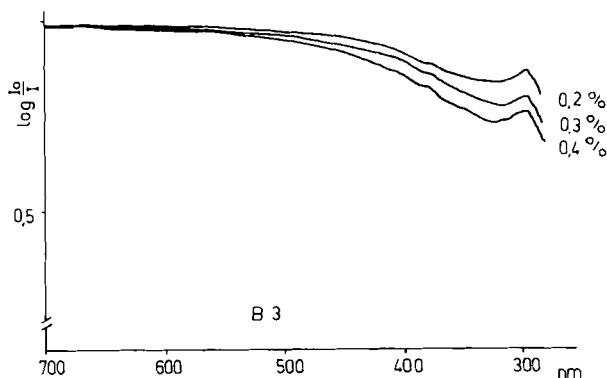


FIG. 5. Change in UV-VIS spectra vs. conversion (fraction B3).

More quantitative results are to be expected from the ozonization reaction by which it is possible to cut the polymer chain into fragments only through the double bonds as proved with PVC samples [13]. The resulting drop in the number-average molecular weight allows one to determine the average number of scissions per polymer chain; this has been used by a few authors to determine the number of double bonds in PVC [8, 14, 15].

We thought the ozonization reaction might be a useful tool to verify our results. Indeed, starting from equally degraded samples the number of scissions per chain should be higher, the shorter the polyene sequences. As a matter of fact, degraded syndiotactic PVC should be expected to exhibit a low number of scissions per chain if, as postulated by our results, part of the double bonds are clustered to form long polyene sequences. Conversely, Bernoullian polymers should give rise to a higher number of scissions per chain because double bonds are more evenly distributed along the chain as shown by UV-visible spectra. This is how it appears to occur according to some preliminary results [9].

The results obtained in this work are shown in Tables 2-4. First of all, there is a noticeable disagreement between molecular weights by GPC and osmometric measurements. Moreover, the discrepancy is higher the more atactic are the fractions. This behavior might be considered to agree with results obtained in a previous work [16], according to which the solution properties of the polymer prepared at a temperature between -25 and $+25^{\circ}\text{C}$, which have a Bernoullian distribution of dyads, are different from those of other polymers deviating from the Bernoullian statistics. It could be possible that these findings are the key to explain the observed differences in the molecular weight determined by osmometry and by GPC.

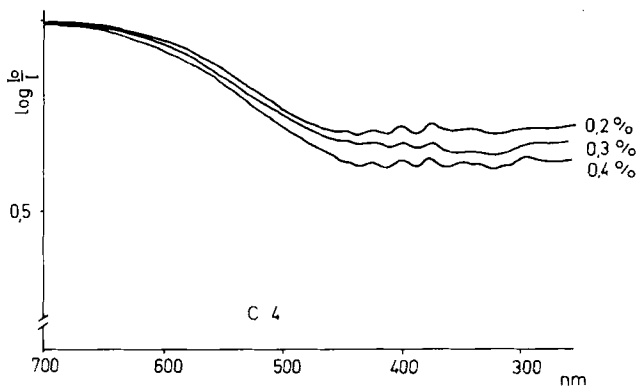


FIG. 6. Change in UV-VIS spectra vs. conversion (fraction C4).

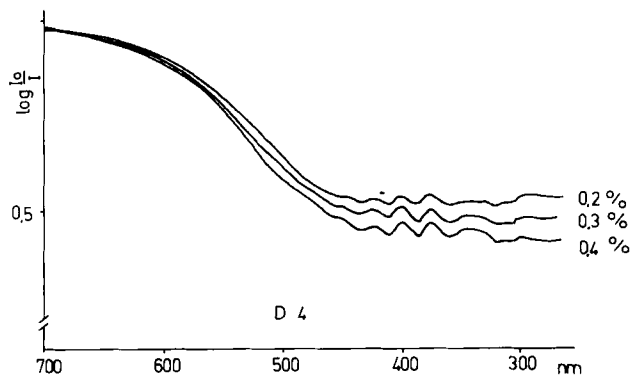


FIG. 7. Change in UV-VIS spectra vs. conversion (fraction D4).

Both methods are reliable for our purposes, as original and ozonized samples are not very different in their overall tacticity.

Table 2 shows the short-time ozonization data for fractions degraded at about 0.1%. The relative values of the number of scissions are very significant. Contrary to what happens with long-time ozonization (Table 3) the number of scissions in samples C and D, which are the most syndiotactic, is high. This may be explained by postulating that ozone first attacks the long polyene sequences, in agreement with what we previously found [9]. The fact that the color of polymer solutions disappears during the first 45 min of ozonization

also accounts for the above statement. Results in Table 2 make it clear most atactic samples undergo numerous chain scissions from the very start of the reaction.

Results obtained in long ozonizations with the same samples as well as with those degraded up to 0.3% (Tables 4 and 5) clearly demonstrate that when ozonization is completed [9], the average number of chain scissions is greater the lower the possibility of syndiotactic sequences along the chain is (the lower conversion of sample A-1 is to be taken into account). This accounts for the occurrence of long polyene sequences in degraded syndiotactic samples which in turn involves a higher propagation in comparison with atactic polymers.

From the above results we can conclude that the influence of syndiotactic sequences on the propagation of degradation, as previously asserted on the basis of both the kinetic data and UV-visible spectra, is well elucidated.

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DISCUSSION

Prof. Braun (Deutsches Kunststoff Institut, Darmstadt, West Germany): I understood from Dr. Martinez's paper and also from his earlier publications that the thermal instability of PVC increases with the number of syndiotactic linkages in the polymer chain. On the other hand, it is known from several published papers and also from practical results that the stability of PVC is slightly increased if the polymer is prepared at lower polymerization temperatures. I think there is a contradiction here which I do not understand. Perhaps the molecular weight has some influence too, as suggested by Dr. Martinez in one of his published papers. I do not understand the difference between increasing syndiotacticity of PVC at lower polymerization temperatures and decreasing thermostability, as Dr. Martinez found, compared with the results of other authors.

Dr. Martinez: The question might be answered by taking into account our previous findings according to which the polymers prepared at temperatures between about -25°C and $+25^{\circ}\text{C}$ have no tactic sequences (Bernoullian distribution), contrary to what happens with the polymers prepared at temperatures lower than -25°C which do not satisfy Bernoullian distribution and therefore have syndiotactic sequences. These latter degrade more quickly and the degraded polymers clearly contain longer polyene sequences than Bernoullian polymers, which accounts for the relative ease of the propagation step.