

# Influence of Tacticity on Thermal Degradation of PVC. V. Relation between the Nature of Labile Conformations and the Polyene Distribution in the Degraded Polymer

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## Synopsis

Four poly(vinyl chloride) (PVC) samples, 1, 2, 3, and 4, were prepared in bulk using 2,2'-azodiisobutyronitrile at 90°C and 60°C and the same initiator together with UV irradiation at 0°C and -50°C, respectively. Fractions were obtained from samples 2, 3, and 4 by extracting with acetone, sample 1 being completely soluble in this solvent. The whole PVC's, as well as their acetone soluble and insoluble fractions, were characterized by determining the intrinsic viscosity, the osmometric molecular weight, and the tacticity; then they were thermally degraded up to conversion of 0.3% in powder state. The values of degradation rate for both the insoluble fractions and the whole PVC's were in agreement with some prior results on the influence of syndiotactic sequences on propagation step. The soluble fractions proved to be very unstable in comparison with the insoluble, which, despite the lower molecular weight of the former, seems to obey their higher content of isotactic conformations. The fine polyene distribution in the degraded polymers was carried out by UV-visible spectroscopy. The results reveal the occurrence of two different polyene distributions, and allow for the peculiar one of the soluble fractions to be related to polyenes consisting of two sequences of trans conjugated double bonds separated by a single cis double bond. The results clearly shows that there are two mechanisms for initiation of the PVC degradation, depending on whether it occurs by random unstable structures or by the normal GTTG isotactic or TTTG heterotactic triads. Moreover, these two initiation processes are proved to give rise to different types of polyenes, which accounts for the occurrence of two unlike mechanisms of propagation.

## INTRODUCTION

Poly(vinyl chloride) (PVC) is known to undergo a dehydrochlorination at temperatures above 100–120°C or upon exposure to ultraviolet radiation.<sup>1,2</sup> As a result, conjugated polyene sequences are formed from the beginning of the reaction, which gives rise to a coloration of the polymer and alters seriously its physical properties. Extensive work has been devoted to characterize the polyenes in degraded PVC by UV-visible spectroscopy. As a general rule, the absorption spectrum is considered to be formed by overlap of the spectra of a mixture of polyenes, which allowed for the different peaks between 250 and 500 nm to be attributed to polyenes of 3–14 double bonds long.<sup>3–7</sup> Nevertheless, a relationship between the shape of the spectrum, that is, the quantitative distribution of polyenes in degraded PVC, and the nature of labile sites or the mechanisms involved in the degradation process has not been stated apart from the assertions that syndiotactic sequences preferably generate long polyenes<sup>8</sup> and that the presence of oxygen results in a shortening of polyenes.<sup>1</sup>

On the other hand, we have recently found that selective nucleophilic sub-

stitution of chlorine atoms in isotactic triads in PVC not only gives enhanced stability but also modifies the UV-visible spectrum in that it shows lesser content of short polyenes than the unsubstituted polymer for very low degradation extents.<sup>9,10</sup> The same result was also found by other authors, who described the substitution reaction with triethyl aluminium although they did not demonstrate which type of chlorine atoms are the more reactive.<sup>11,12</sup>

Therefore, it appears as though the type of polyene distribution depended, to a certain extent, on the content of labile conformations in PVC. In order to make clear such a dependence, the differences in polyene distribution found for degraded fractions from PVC samples of different tacticity are studied in the present work, as a new approach to the knowledge of the degradation processes in PVC.

## EXPERIMENTAL

### Preparation of Polymers and Fractions

Samples 3 and 4 were prepared by bulk polymerization using 2,2'-azodiisobutyronitrile and UV irradiation to initiate polymerization at temperatures of 0°C and -50°C, respectively. The full details have already been published.<sup>13</sup> Samples 1 and 2 were prepared at 90°C and 60°C, respectively, by the same method except for the UV irradiation, which was not used.<sup>13</sup>

For the fractions, 20 g of PVC were allowed to stir for 24 h with 2 L of acetone in a thermostated vessel under nitrogen atmosphere. After separation of the insoluble fraction by centrifugation, the soluble fraction was precipitated with methanol and then washed and dried at 40°C. The insoluble fraction was also washed and dried at 40°C.

### Characterization of Polymers and Fractions

The viscosities were measured at 30°C with 10 g/L solution in cyclohexanone using a Fica automatic viscosity meter.

The osmometric measurements were carried out at 34°C with solutions in cyclohexanone using a Knauer membrane osmometer.

The tacticities were calculated from a correlation between IR absorbance ratio  $A_{1428\text{ cm}^{-1}}/A_{1434\text{ cm}^{-1}}$ , which is a measure of the syndiotactic content,<sup>14</sup> and the conditional probabilities calculated by <sup>13</sup>C-NMR of steric placements on polymers prepared under the same conditions as those of samples 1, 2, 3, and 4 as published elsewhere.<sup>15</sup> According to this correlation, samples 1 and 4 are clearly not Bernoullian in character; the isotactic placement is favored in the former while the syndiotactic placement is favored in the latter. Samples 2 and 3 are rather Bernoullian with a slight tendency towards isotacticity and syndiotacticity, respectively.

In order to make clear the differences in tacticity between the soluble and insoluble fractions, the regions 600-700 cm<sup>-1</sup> and 1400-1500 cm<sup>-1</sup> of the spectra of fractions from sample 2 are reproduced in Figure 1.

Data concerning the preparation and characterization of both the polymers and their fractions are summarized in Tables I and II.

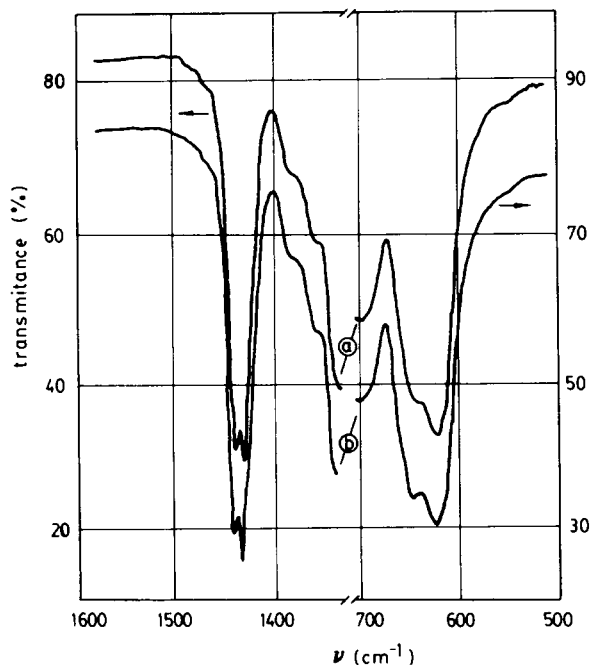


Fig. 1. IR spectra of fractions from sample 2 (regions 600–700  $\text{cm}^{-1}$  and 1400–1500  $\text{cm}^{-1}$ ): (a) soluble fraction in acetone; (b) insoluble fraction in acetone.

### Thermal Degradation

The thermal degradation at 180°C of the PVC samples and their fractions was followed by a conductimetric method as described elsewhere.<sup>16</sup> The slope of the linear part of isotherms is taken as the degradation rate (Table III).

TABLE I  
Characteristics of Polymers

Sample	$[\eta]$ (mL/g)	$\bar{M}_n \times 10^{-3}$	$A_{1428}/A_{1434}$	$\rho^a$
1	40.0	18.0	1.05	1.09
2	74.3	40.0	1.10	1.04
3	253.0	85.0	1.22	0.95
4	196.6	53.0	1.42	0.92

<sup>a</sup> Persistence ratio from  $^{13}\text{C}$ -NMR.<sup>14</sup>

TABLE II  
Characteristics of Fractions

Sample	Extraction with acetone (%)		$[\eta]$ (mL/g)		$\bar{M}_n \times 10^{-3}$	$A_{1428}/A_{1434}$	
	Soluble fraction (S)	Insoluble fraction (I)				S	I
			S	I			
1	100.0	—	40.0	—	18.5	1.05	—
2	26.8	73.2	42.2	75.0	14.0	1.06	1.11
3	2.5	97.5	36.8	254.0	14.5	1.13	1.25
4	2.4	97.6	48.4	196.6	14.0	1.35	1.42

### Ultraviolet-Visible Spectra

The spectra of all degraded samples were recorded with solutions of 4 g/L in hexamethylenphosphortriamide using a Perkin-Elmer 554 spectrometer at 40°C in an inert atmosphere.

### RESULTS AND DISCUSSION

As illustrated by the values of the IR absorbance ratio  $A_{1428\text{ cm}^{-1}}/A_{1434\text{ cm}^{-1}}$ , the persistence ratio ( $\rho$ ), and the viscosities and osmometric molecular weight (Table I), the starting PVC samples are different in that, on the one hand, the isotactic content decreases strongly from sample 4 to sample 1<sup>15</sup> and, on the other, samples 1 and 2, that is, the more isotactic ones, happen to have the lower molecular weight. As to the fractions obtained by extracting with acetone (Table II), two features deserve mention: (i) The extracted amount decreases markedly when the overall syndiotactic content increases and (ii) the viscosity of the soluble fractions is lower than that of both the insoluble fractions and the whole PVC samples. Conversely, the isotactic content of the soluble fractions is significantly higher, as shown by the values of IR absorbance ratio  $A_{1428\text{ cm}^{-1}}/A_{1434\text{ cm}^{-1}}$  (Table II) and by spectra of fractions from sample 2 in Figure 1. Actually, both  $A_{1428\text{ cm}^{-1}}/A_{1434\text{ cm}^{-1}}$  and  $A_{640\text{ cm}^{-1}}/A_{685\text{ cm}^{-1}}$  IR absorbance ratios are known to be a relative measure of the syndiotactic content in PVC.<sup>14</sup> Should this method not be very sensitive, the spectra of Figure 1 clearly indicate that the above-quoted absorbance ratios markedly decrease from the insoluble fraction to the soluble, which accounts for the latter fraction having a higher content of isotactic configuration. Furthermore, the values of the IR absorbance ratio  $A_{1428\text{ cm}^{-1}}/A_{1434\text{ cm}^{-1}}$  for the insoluble fractions correspond either to a Bernoullian polymer (sample 2) or to a clearly syndiotactic polymer (sample 3 and especially sample 4),<sup>15</sup> which makes it reasonable to think that the isotactic conformations extracted with acetone are the ones which make the whole sample 1 and, to a lesser extent, sample 2, to behave as non-Bernoullian isotactic polymer. As indicated by some works of ours on selective substitution on PVC, the extracted isotactic conformation could very well be the triad GTTG, which is the least probable among all the possible isotactic triads.<sup>9,10</sup> In support of this assertion is the decrease of the acetone soluble fraction with increasing syndiotacticity of the whole polymer (Table II). Be that as it may, the acetone soluble parts appear to consist of a very specific isotactic structure, the percentage of which increases with increasing temperature of polymerization. Moreover, the

TABLE III  
Values for Thermal Degradation at 180°C

Sample	Degradation rate $\times 10^3$ ( $[\text{ClH}]/[\text{ClH}]_0 \cdot \text{min}^{-1}$ )		
	Whole polymer	$S^a$	$I^b$
1	12.5	—	—
2	3.6	5.7	3.4
3	5.5	34.3	6.2
4	10.3	41.1	12.6

<sup>a</sup> Soluble fraction.

<sup>b</sup> Insoluble fraction.

above-quoted results on substitution reaction on PVC<sup>9,10</sup> and the differences in tacticity between the insoluble and the soluble fractions clearly suggest the specific isotactic structure of the soluble fractions to be preferably formed by GTTG triads.

From the above considerations it follows that the differences in degradation behavior of the soluble fractions in comparison with the insoluble must be attributed either to the molecular weight or to the isotactic configuration.

The degradation rates obtained at 180°C in solid state for the four PVC samples and their fractions are given in Table III. The values corresponding to the whole polymers are in line with our prior findings that Bernoullian polymers are more stable than the non-Bernoullian regardless of the tendency towards syndiotacticity or isotacticity of the latter. In the case of high syndiotactic content, the instability was proved to be due to a favored polyene growth, which results in an enhanced propagation. On the contrary, no definite conclusions were obtained for the rather isotactic polymers, although the fact that their behavior, in terms of either polyene distribution or number of chain scissions by ozonolysis, lies between that of Bernoullian and syndiotactic polymers suggested the occurrence of a higher number of initiation sites which might result in propagations close to each other.<sup>17</sup>

As shown in Table III, acetone-soluble fractions degrade at much higher rate than insoluble fractions. Moreover, the difference in degradation rate increases with increasing syndiotacticity of the starting PVC. Taking into account that soluble fractions are scarcely different in viscosity (Table II), the latter results might be accounted for by the presence in the soluble parts of the above-indicated specific fraction of isotactic conformations which would involve a high concentration of initiation sites.<sup>9,10</sup> On the other hand, the content of syndiotactic sequences increases from sample 1 to sample 4 (Table I), which, as previously demonstrated, involves a parallel increase of degradation rate because of the syndiotacticity effect on the propagation step.<sup>8</sup>

In conclusion, the soluble fractions behavior seems to obey in principle two cooperative effects: that of the specific isotactic placements extracted with acetone and that of a favored propagation due to the presence of syndiotactic sequences. This latter effect is expected to be important for samples 3 and 4, which accounts for their very high degradation rate. On the contrary, only the former effect is to be considered for sample 2 because of its almost Bernoullian character.<sup>15</sup>

The low molecular weight has also been claimed to increase the degradation rate,<sup>16,18</sup> but it was proved not to modify the polyene distribution.<sup>16</sup> For the soluble fractions in Table II the number average molecular weights are not much unlike while, as demonstrated below in this work, the polyene distribution is quite different from that of insoluble fractions. These features allow us to think that the enhanced instability of soluble fractions are mainly due to the above-discussed tacticity effects even if a certain contribution of the molecular weight to the overall degradation rate cannot be ruled out.

It appears most interesting to relate the above differences in degradation rate to the various types of polyene distribution found by UV-visible spectroscopy for the degraded fractions in Table III. Figures 2, 3, and 4 show the absorption spectra of PVC samples 2, 3, and 4 and of their acetone-soluble and -insoluble fractions, respectively. The degradation extent was fixed at 0.3% for all the

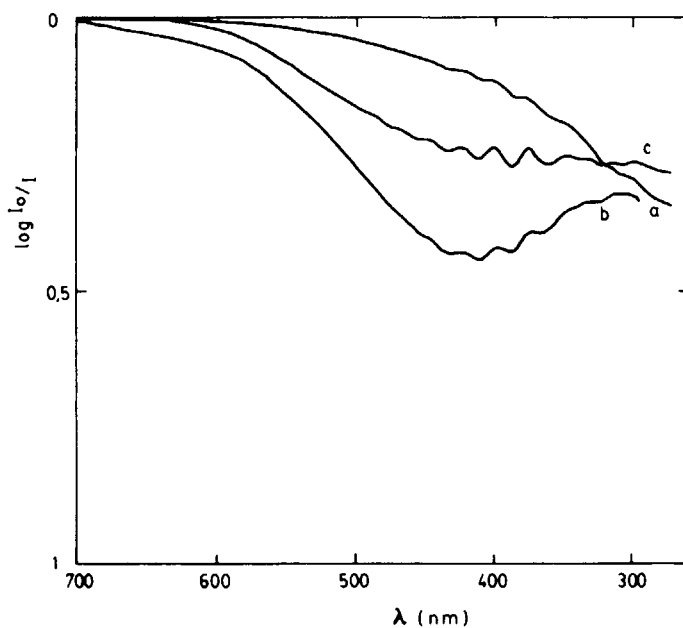


Fig. 2. UV-visible absorption spectra of sample 2 degraded to 0.3% at 180°C in solid state: (a) whole polymer; (b) soluble fraction in acetone; (c) insoluble fraction in acetone.

experiments. Unexpectedly, the whole PVC and its fractions, after degradation, are very different in polyene distribution and the differences are the greater as the overall isotactic content increases (Fig. 2). The shape of the absorption

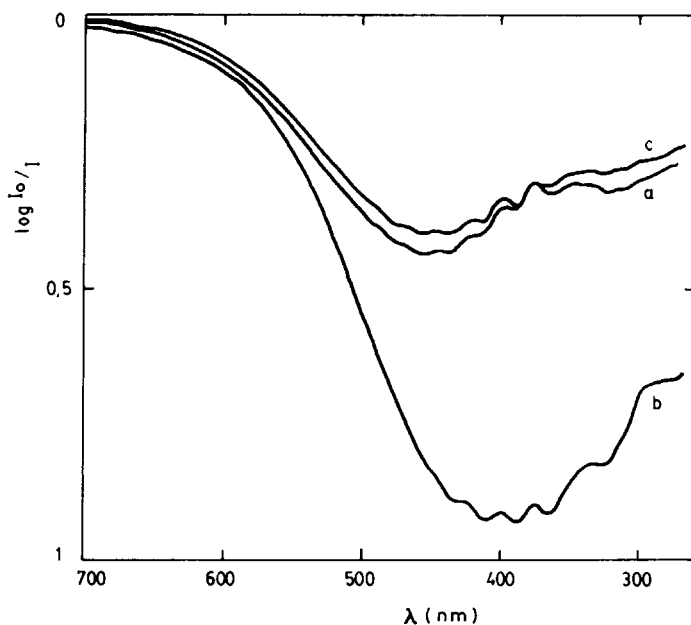


Fig. 3. UV-visible absorption spectra of sample 3 degraded to 0.3% at 180°C in solid state: (a) whole polymer; (b) soluble fraction in acetone; (c) insoluble fraction in acetone.

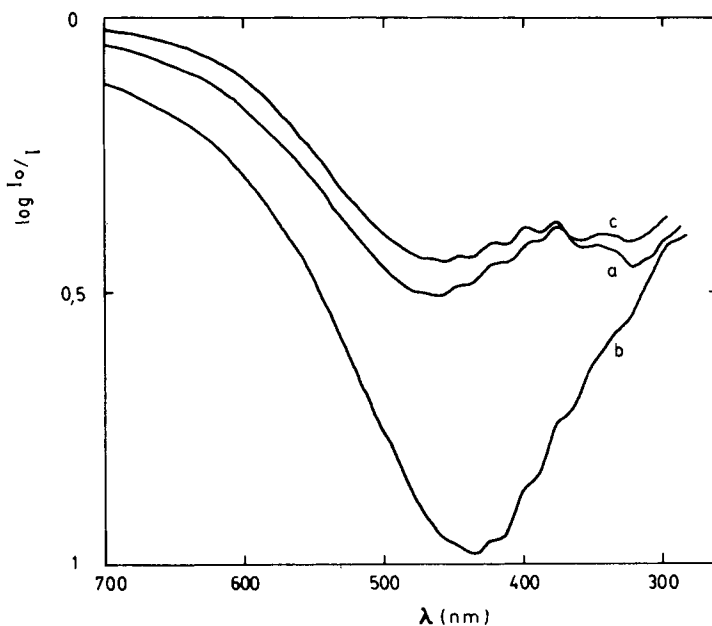


Fig. 4. UV-visible absorption spectra of sample 4 degraded to 0.3% at 180°C in solid state: (a) whole polymer; (b) soluble fraction in acetone; (c) insoluble fraction in acetone.

spectrum is alike for all the soluble fractions. It indicates an enhanced concentration of polyenes of 7–9 double bonds ( $\lambda$  between 388 and 434 nm) relative to both the long and the short polyenes. This rather narrow distribution of polyenes, together with the high intensity of the maxima, is at variance with the fact that the spectrum is considerably flatter than that of insoluble fractions, which suggests the polyenes from soluble fractions to be different in nature from those from insoluble fractions. This is confirmed by some of the results shown later in this work.

The shape of the spectra of degraded insoluble fractions (Figs. 2–4) is in good agreement with the above-quoted results on the influence of the syndiotacticity on polyene distribution in degraded PVC,<sup>8</sup> and so it is for the spectra of degraded PVC samples 2, 3, and 4. Nevertheless, it is worth noticing that in the latter spectra the short polyenes/long polyenes ratio is higher than in the case of insoluble fractions and that this difference is much accentuated for sample 2, that is, the one which exhibits the higher soluble fraction (Table II). These results are in line with the conclusions above drawn from degradation data that suggest the soluble fractions consist of a definite type of isotacticity which, as indicated by data in Table II, might be concomitant with the low molecular weight.

That the presence of the soluble fraction is the main degradation determining factor in PVC is clearly illustrated by the spectra in Figures 2, 3, and 4, together with the values obtained for degradation rate (Table III). Indeed, the degradation behavior of samples 3 and 4 is rather like that of their respective insoluble fractions in terms of both the degradation rate (Table III) and the polyene distribution (Figures 3 and 4). Moreover, the slightly higher degradation rate and the somewhat lower short polyenes/long polyenes ratio for the latter fractions are doubtless due to their higher syndiotactic content (Table II).<sup>15</sup> Conversely,

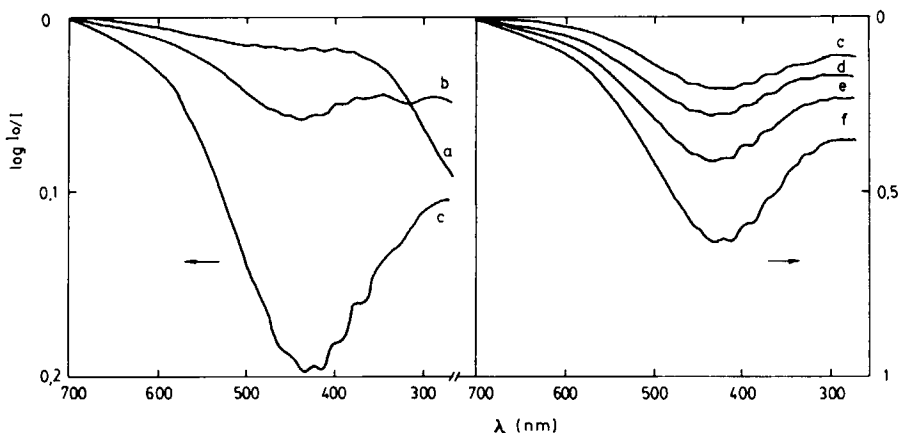


Fig. 5. Variation of the UV-visible spectrum of sample 1 with the degradation extent in solid state: (a) 0.01%; (b) 0.02%; (c) 0.05%; (d) 0.1%; (e) 0.2%; (f) 0.3%.

in the case of sample 2 the short polyenes/long polyenes ratio is much higher for the whole polymer (Fig. 2) and the stability values are reversed (Table III). On the basis of these results, the instability of PVC appears to be proportional to its fraction soluble in acetone.

In order to clarify the nature of such influence, a set of degradations was carried out with PVC sample 1, which is entirely soluble in acetone. Degradation extents between 100 ppm and 3000 ppm were chosen to follow the evolution of the UV-visible spectra. The results, as displayed in Figure 5, reveal that at very low degradation extent the polyenes formed are short, but from, as far as the degradation progresses, the concentration of polyenes of 7–9 double bonds, that is, those which are responsible for the peculiar absorption bands of the soluble fractions, increases greatly at the expense of the short.

Whether this effect occurs with whole PVC samples or not depends on the overall isotactic content and on the percentage of degradation. Actually, commercial polymers have been reported to give rise to UV-visible spectra somewhat similar to that of sample 1 but they were considered to result from the occurrence of normal long polyenes.<sup>11,12</sup>

The above-discussed results (Figs. 2–5) make it clear that, as a general rule, the overall degradation of a PVC sample consists of two different processes that overlap with each other and whose main feature is that the polyene distribution is like that of the soluble fraction and that of insoluble fraction respectively.

The fact that the spectra in Figures 2–4 are not additive indicates that the polyenes characteristic for each of either type of distribution are also different in nature.

In support of the above assertions is the fact that mixtures of degraded polymers having especially either the specific absorption between 388 nm and 434 nm or absorption at about 280–300 nm gave UV-visible spectra totally additive as shown in Figure 6. Therefore, the progressive increase of the absorption at 388–434 nm at the expense of that at 280–300 nm with increasing degradation (Fig. 5) may be explained by assuming that no sooner have the short polyenes been formed through specific dehydrochlorinations, then the propagation occurs preferably from them in the soluble fractions.



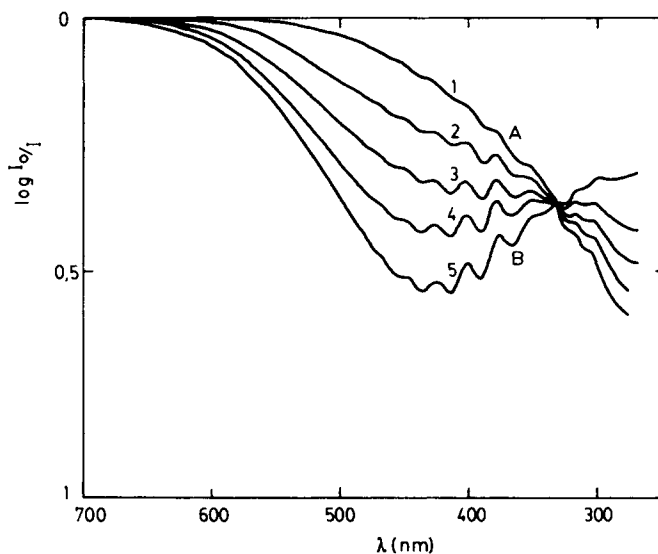


Fig. 6. UV-visible spectra of mixtures of 0.3% degraded samples A (Bernoullian polymer) and B (Commercial polymer) (concn 4.8 g/L): [B] (%): (1) 0; (2) 25; (3) 50; (4) 75; (5) 100.

On the contrary, the shape of spectra of degraded insoluble fractions was not found to change with increasing degradation extent.

That the evolution of the UV-visible spectra with degradation for the soluble fractions is independent of the molecular weight was demonstrated by some prior works.<sup>16</sup> Hence, the participation of the acetone soluble fractions in the degradation process is to be attributed to their specific isotacticity.

In connection with this, a mechanism for the evolution of the UV-visible spectra of soluble fractions and hence for the degradation of PVC may be put forward as follows. The two lateral chlorine atoms in the isotactic GTTG triad and one of the lateral chlorine atoms in the heterotactic TTTG triad have been proved to be less stable to the initiation of degradation than the others in PVC.<sup>9,10</sup> The initiation by such conformations leads preferably to the formation of a cis double bond.<sup>19</sup> Conversely, the remain conformations in PVC, whether they be isotactic or syndiotactic diads, are likely to give rise to trans double bonds exclusively. Consequently, the subsequent dehydrochlorinations by both sides of the initial cis double bonds should give rise to polyenes consisting of a cis double bond flanked by two sequences of conjugated trans double bonds, regardless of the propagation mechanism.<sup>2,20</sup>

In our opinion, the so-resulting polyenes are quite different in nature from the all-trans ones which arise from initial trans double bonds as formed by random initiations at sites other than the two above-considered conformations. That would allow for the former polyenes to be related to the shape of the absorption spectra of the soluble fractions while the spectra of the insoluble fractions would be characteristic for the all-trans polyenes (Figs. 2-5).

The above-proposed attribution of the absorption bands at 388-434 nm for the soluble fractions is supported by a few works in the literature on the absorption spectra of stereoisomeric structures of some carotenoids.<sup>21,22</sup> According to them, the all-trans isomers and the all-cis isomers are characterized by a fine

and a flat absorption spectrum, respectively, in the visible region and the spectrum of the trans isomer with a single central double bond of cis structure is almost similar in intensity to that of the all-trans isomer but somewhat flatter in character. These conclusions were confirmed experimentally for a series of polyene isomers and are in perfect agreement with theoretical predictions.<sup>21</sup>

The results in the present work enable us to conclude the spectra of soluble fractions to be characteristic for a very narrow polyene distribution in which the concentration of either long polyenes (over 10 double bonds) or short polyenes (below 6 double bonds) is very low relative to that of polyenes of 7–9 double bonds. On the contrary, the shape of the spectra of insoluble fractions indicates clearly a much larger distribution with a considerable contribution of the long and the short polyenes. Furthermore, the above-quoted works on the visible spectra of carotenoids<sup>21</sup> make it reasonable to assume the occurrence of our above suggestions that the polyenes in the degraded soluble fractions consist of two sequences of trans-conjugated double bonds separated by a single cis double bond, which, in its turn, would arise from specific dehydrochlorinations through GTTG isotactic triad or TTTG heterotactic triad conformations.<sup>9,10</sup>

In conclusion, and even if more details about this subject will be given in further works now under way, the above results reveal new data in support of our previous assertions that some normal isotactic conformations are responsible, to a great extent, for both the thermal degradation rate and the coloration process.<sup>9,10</sup> Moreover, they provide with a further approach to the knowledge of the very mechanism of degradation of PVC insofar as they state, on the one hand, that the initiation occurs through the GTTG isotactic triads as well as through the widely studied abnormal labile structures, and, on the other, that the nature of the polyenes resulting from both initiations is different in that, as discussed above, initiation by the isotactic triads brings about the formation of polyenes which consist of a cis double bond flanked by two sequences of trans double bonds. Consequently, the mechanisms for both initiation and propagation are shown to be related to the fraction of GTTG isotactic triad, which is present in the polymer.

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