Influence of Tacticity on the Thermal Degradation of PVC. VI. New Advances in the Degradation Process through the Behavior of Modified PVC Samples

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Synopsis

Three PVC samples having different tacticities, as well as the products resulting from their reaction with sodium thiophenate, which was previously found to occur selectively by some definite isotactic conformations, were degraded at 180°C in solid state up to 0.3%. In agreement with prior works, the stability of the substituted polymers was shown to be higher as the substitution extent increased up to a definite value, which depends on the overall isotactic content of the starting materials. On the other hand, the found changes in polyene distribution for the degraded samples with the substitution extent, as followed by UV-visible spectroscopy, demonstrate that the specific bands at 393, 416, and 437 nm, which are known to be characteristic for the most unstable PVCs, arise from the lability of some chlorine atoms located at GTTG′ (or TTTG) conformations, as prior results suggested. On the basis of the so-obtained correlation between the content of some isotactic triads (especially the GTTG′) and both the thermal instability and the formation of the above-indicated specific polyenes, new advances in the degradation mechanism are proposed.

INTRODUCTION

Selective substitution of the central chlorine atoms in some isotactic triads conformations in PVC, by nucleophiles like sodium thiophenate, was proved to result in an enhanced thermal stability as well as an increase of the short polyenes/long polyenes ratio in the degraded polymer.[1,2] On the other hand, it has been shown recently that the content of specific polyenes of seven to nine double bonds (λ between 390 and 440 nm in UV-visible spectra) relative to that of either long polyenes (over 10 double bonds) or short polyenes (below six double bonds), in degraded PVC, is higher as the isotactic content of the polymer increases.[3]

Since the conformations involved in the selective substitution are the isotactic GTTG′ and the heterotactic TTTG,[1,2] the study of the influence of substitution extent on both the thermal stability of the modified polymers and the polyene distribution in the same polymers after degradation proves to be an excellent way to know whether the above-quoted behavior of unmodified PVC is or is not due to the GTTG′ and TTTG conformations. In case it was, a definite approach to the knowledge of the degradation mechanisms for PVC would have been done.

This work is dealing with such a study by using three PVC samples having very different tacticities, before and after substitution at various conversions.

EXPERIMENTAL

Preparation of Polymers. Samples 1 and 2 were prepared by bulk polymerization at 90°C and 60°C, respectively, using 2,2′-azodiisobutyronitrile as

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TABLE I
Characteristics of Polymers

Polymer	$\overline{M}_n \times 10^{-3}$	$\dfrac{A_{1428\ cm^{-1}}}{A_{1434\ cm^{-1}}}$[a]	P(SS)	P(SI&IS)	P(II)[b]
1	21.5	1.05	0.296	0.490	0.214
2	38.9	1.10	0.311	0.495	0.194
3	85.0	1.22	0.378	0.468	0.154

[a] Syndiotacticity/isotacticity ratio from IR spectra.[3]
[b] Fraction of syndio-, hetero-, and isotactic triads.[3]

initiator. Sample 3 was prepared by the same method but using UV irradiation to initiate polymerization at 0°C. The full details have already been published.[4]

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

The tacticities were measured by means of the ^{13}C-NMR spectra obtained at 20.1 Mhz and 100°C using a WP-80 Bruker Spectrometer. The polymers were examined as a 10% solution in a $\frac{1}{4}$ mixture of deuterated dimethylsulfoxide and o-dichlorobenzene; 10-mm sample tubes were used. The calculations were carried out by measuring the areas with a compensating polar planimeter. The obtained values are given in Table I.

Substitution Reaction. The PVC samples were treated at −30°C with sodium thiophenate in purified cyclohexanone as solvent. The experimental procedure was described previously.[1] The chosen samples (Table II) were drawn at the indicated reaction times for the three polymers. The conversion extents were determined both by microanalysis and by measuring the thiophenate band at 256 nm in the UV-visible spectra and applying the calibration curve before established.[1]

Thermal Degradation. All the samples were degraded up to 0.3% in solid state at 180°C. The process was followed by a conductimetric method as described previously.[4] The slope of the linear part of isotherms is taken as the degradation rate (Table III).

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.

To measure the band at 256 nm for the thiophenate modified samples, the spectra were recorded with solutions of 0.8 g/L in tetrahydrofuran.

RESULTS AND DISCUSSION

Substitution data in Table II show that the higher the syndiotactic content, the lower is the substitution extent at any reaction time. This is expected to be so because, within the reaction period considered, the substitution reaction was demonstrated to occur selectively by isotactic GTTG' and heterotactic TTTG conformations,[1] whose content obviously decreases from polymer 1 to polymer 3 (Table I).

On the basis of these tacticity data, unmodified samples 1, 2, and 3, after a similar degradation, were expected to exhibit markedly decreasing content of

TABLE II
Substitution Reaction Data

Modified samples	t (h)	Conversion (%)		
		Polymer 1	Polymer 2	Polymer 3
0	0	0	0	0
1	0.5	0.52	0.36	0.07
2	2	0.68	0.49	0.12
3	6	0.76	0.64	0.21
4	14	0.95	0.78	0.25
5	47	1.20	1.00	0.42
6	94	1.34	1.08	0.52
7	167	1.49	1.30	0.62
8	340	1.90	1.69	1.05

the specific polyenes of seven to nine double bonds, i.e., decreasing contribution of absorptions between 390 and 437 nm in the UV-visible spectra.[3] As later discussed, the comparison of spectra (a) in Figures 1, 2, and 3 shows it to be so. Consequently, the fact that samples 1, 2, and 3 are different in substitution behavior (Table II) as well as our prior finding that substitution under the used experimental conditions, only affects some isotactic triads,[1,2] account for the changes which are now observed in polyene distribution of substituted polymers after equal degradation (spectra b–d in Fig. 1), to be due to the isotactic parts in the starting polymers. As shown below, these results prove to be very illustrative for the understanding of the degradation process.

Degradation data in Table III show that the selective substitution in sample 1 brings about a strong progressive stabilization until a substitution extent of 0.76% is attained; afterward the stability decreases with increasing substitution. These effects were proposed to result respectively from the lability of some chlorine atoms located at GTTG′ and TTTG conformations, which disappear by selective substitution[1,2] and from the favored building-up of all-trans polyenes upon initiation at syndiotactic sequences. Actually, specific substitution at GTTG′ and TTTG triads yields an increase in overall trans chain conformation.[1,2]

The above behavior is also observed for samples 2 and 3, but the stabilizing

TABLE III
Values for Thermal Degradation at 180°C

Modified samples	Degradation rate $\times 10^3$ ([HCl]/[HCl]$_0 \cdot$ min^{-1})		
	Polymer 1	Polymer 2	Polymer 3
0	12.6	3.3	5.5
1	12.1	2.9	5.0
2	8.9	2.8	4.9
3	5.7	2.9	—
4	—	3.2	5.4
5	—	—	5.8
6	—	4.8	6.8
7	7.8	5.2	8.6
8	9.5	6.1	11.1

effect is achieved at substitution extents of 0.49% and 0.12%, respectively (Tables II and III). Taking into account the relative content of isotacticity for the three samples (Table I), these results clearly confirm that the substitution affects selectively the above-mentioned conformations.

On the other hand, it is worth noticing that the relative improvement in stability decreases markedly from sample 1 to sample 3, that is, with decreasing content of GTTG' and TTTG conformations. This is well illustrated by the values for the degradation rate ratios, 5.7/12.6 = 0.45 (sample 1), 2.8/3.3 = 0.85 (sample 2), and 4.9/5.5 = 0.89 (sample 3), which are a relative measure of the stabilizing effect (Table III). These results make it clear that the substituted structures in the polymer, that is, isotactic GTTG' and heterotactic TTTG triads,[1,2] contain labile chlorines. Hence, any change in the overall degradation behavior of the modified samples relative to the starting polymers should be attributed to such conformations.

The above discussion has been made on the assumption that the substituted fraction of isotactic and, to a lesser extent, heterotactic triads, contains preferably GTTG' and TTTG conformations, as suggested by the kinetics and mechanisms of substitution.[1,2] The true contribution of these conformations to the overall isotactic, heterotactic, and syndiotactic triads cannot be experimentally measured. Nevertheless, it can be estimated approximately by taking into account the bond rotational probabilities $P(T)$, $P(G)$ for each of the nonterminal bonds in trichloroheptane as recently calculated by Tonelli et al.[5] Assuming that the three samples are Bernoullian (Table I) and taking into consideration Tonelli's values,[5] the probability $P(GTTG) = P(G)_2 P(T)_3 P(T)_4 P(G)_5$ (where figures refer to the bonds in the triad) of the occurrence of a GTTG' conformation would be 0.128, 0.0037, and 0.012 for the isotactic, syndiotactic, and heterotactic triad, respectively. With respect to the TTTG conformation, the probabilities $P(TTTG) = P(T)_2 P(T)_3 P(T)_4 P(G)_5$, would be 0.092, 0.052, and 0.22, respectively, for the same triads.

Consequently, on the basis of the tacticity data in Table I, the GTTG' conformation content must be assumed to decrease markedly from sample 1 to sample 3 and the TTTG conformation content to be similar for samples 1 and 2, and significantly lower for sample 3.

In connection with the decrease in stability with substitution extent after the initial stabilizing effect (Table III), two complementary consequences of the substitution are worth mentioning. On the one hand, the nucleophilic substitution on the central carbon atom of the GTTG' isotactic triad makes the two gauche conformations to adopt a transconformation. On the other, the substitution might be thought to enhance the lability of the chlorine atoms close to a substituted unit. As discussed later, the former statement is clearly supported by the UV-visible spectra of degraded polymers (Figs. 1–3) as well as by the previously found influence of TT conformations on the propagation of polyenes.[6] The latter statement is more difficult to explain. However, it is worthy of note that the configurational inversion resulting from an S_{N^2} substitution on the central atom of a heterotactic TTTG conformation, is expected to involve, on the one hand, the appearance of a new trans conformation at the expense of the initial gauche one (as is the case for the GTTG' triad on either side), and, on the other, the occurrence of a new gauche conformation on the syndiotactic side. Consequently, both a polyene building-up effect and the formation of a new labile
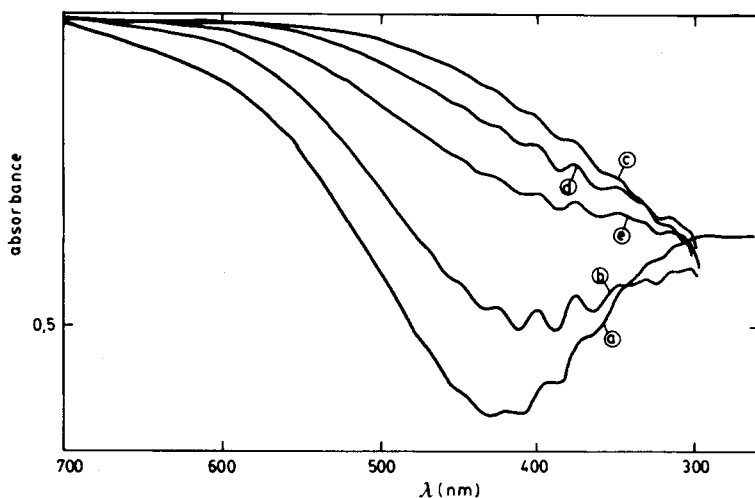
Fig. 1. UV visible absorption spectra of modified sample 1 degraded to 0.3% at 180°C in solid state: (a) 0%; (b) 0.52; (c) 0.76%; (d) 1.49%; (e) 1.90%.

chlorine could be suggested to result from a single substitution on the central carbon atom of a TTTG heterotactic triad. Further results on these subjects will be given in forthcoming papers.

Figures 1–3 exhibit the evolution of the UV-visible spectra with substitution extent for degraded samples 1, 2, and 3, respectively, and their corresponding substituted products. All the spectra were recorded from equally degraded samples (0.3%).

From the comparison of spectra in Figure 1, it immediately follows, on the one hand, that unmodified sample 1 gives rise to an enhanced absorption at 393, 416, and 437 nm, which quickly vanishes with the substitution extent, and, on the
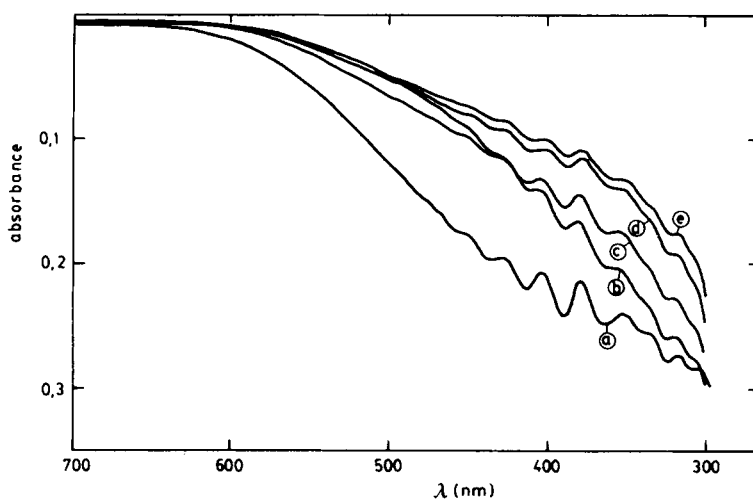

Fig. 2. UV-visible absorption spectra of modified sample 2 degraded to 0.3% at 180°C in solid state: (a) 0%; (b) 0.49%; (c) 0.78%; (d) 1.08%; (e) 1.69%.
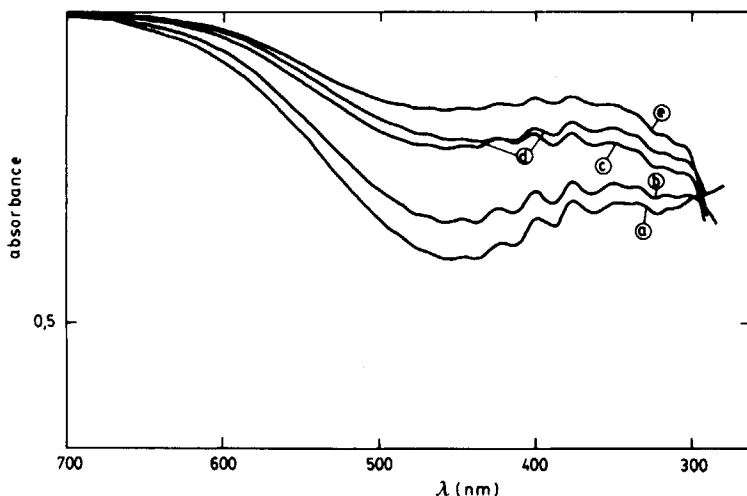
Fig. 3. UV-visible absorption spectra of modified sample 3 degraded to 0.3% at 180°C in solid state: (a) 0%; (b) 0.07%; (c) 0.21%; (d) 0.52%; (e) 1.05%.

other, that the short polyenes/long polyenes ratio increases from spectrum "a" to spectrum "c," that is, as far as the stabilizing effect of substitution is occurring (Table III); afterward, the above ratio starts decreasing with substitution (spectra d–e). The former effect was also observed for a series of unmodified PVC samples with decreasing isotactic contents, which suggested the anomalous absorptions between 390 and 440 nm to be related to isotactic structures.[3] The latter effect is the one which was demonstrated to result from a favored propagation along trans syndiotactic sequences, which, as above mentioned, increases the overall degradation rate.[1,2] It becomes apparent when the syndiotactic content exceeds the value characteristic for a Bernoullian tacticity distribution.[6]

It is worthy of note that this increase in long polyenes content affects all the polyenes that absorb from about 400 nm,[6] while the occurrence of high specific absorptions at 393, 416, and 437 nm, without noticeable increase of the other bands taking place, is only observed for polymers with isotactic content higher than that of Bernoullian tacticity distribution.[3] This correlation between isotactic triads and the bands at 393, 416, and 437 nm is now demonstrated by the fact that the latter bands disappear as the specific substitution of isotactic triads take place (Fig. 1, spectra a–c).

The above results clearly reveal that, as previously shown with unmodified samples,[3] there exist two well-differentiated types of UV-visible spectra of degraded PVC: that of spectra containing specifically high absorptions at 393, 416, and 437 nm [Fig. 1(a)] and that of spectra c–e (Fig. 1) consisting of a large long polyene distribution relative to the former spectra. Moreover, taking into account the selectivity of the substitution reaction,[1,2] the absorptions between 390 and 440 nm are demonstrated to be due to polyene arising from initiations at the specific GTTG′ isotactic and, to a lesser extent, TTTG heterotactic triads, which are therefore proved to be very labile structures in PVC.

In agreement with the above statements, the spectra of Figure 2 show a significantly lower contribution of the bands at 393, 416, and 437 nm (only spectrum

"a" exhibits a slightly accentuated overall absorption in this region). Actually, the content of GTTG' and TTTG conformations in sample 2 is markedly lower than in sample 1 (Table I), which explains that the contribution of the above bands is not great enough for being noticeable.

As expected from the very low content of isotactic conformations for sample 3 (Table I), all the spectra of Figure 3 are rather similar in shape; hence, no contribution of bands at 393, 416, and 437 nm is observable.

In conclusion, the whole results in this work provide us with new advances in the knowledge of both the reasons for the instability and the mechanism of degradation of PVC in terms of initiation and propagation steps. Actually, they make evident, on the one hand, the occurrence of some normal conformations in PVC, especially the GTTG' isotactic triad, which are labile relative to the remaining structures, and, on the other, that the initiation of degradation by such conformations brings about a definite type of polyenes that absorbe at 393, 416, and 437 nm.

With reference to the latter polyenes, it is of great interest to know whether they contain or not cis double bonds as suggested elsewhere.[3] Nevertheless, the present stage of the problem prevents us from drawing a definite conclusion. Be that as it may the found correlation between the absorptions at 393, 416, and 437 nm, and both the presence of isotactic triads and the instability of PVC, accounts for these isotactic triads to be assumed as the main structures which govern the degradation process in PVC.

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