Influence of tacticity on the thermal degradation of PVC: 8. A comprehensive study of the local isotactic $GTTG^-$ conformation dependence of the mechanism of initiation

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Some new attempts to demonstrate the superiority of the $GTTG^-$ conformation of isotactic triads relative to other labile structures containing allylic or tertiary chlorine in inducing the thermal degradation of poly(vinyl chloride) (PVC) are presented. They concern: (i) the degradation of polymers after nucleophilic substitution in two types of solvent involving the removal of the $GTTG^-$ arrangement in a quite different way; (ii) the degradation of PVC blends with a few additives which, as proved by Fourier transform infrared (*FT*i.r.) spectroscopy, are able to interact specifically with the *mmr* structure adopting $GTTG^- TT$ conformation at the end of isotactic sequences; (iii) the degradation of PVC after the disappearance of $GTTG^-$ conformations as a result of the $GTTG^- TT \Rightarrow GTGTTT$ irreversible conformational change provoked by stretching of films at temperatures near the glass transition; and (iv) the degradation of PVC after *FT*i.r. checked changes in content of $GTTG^-$ conformation, induced by annealing at temperatures between 70 and 120°C. The correlations so obtained give evidence of the PVC thermal-instability-determining role of the $GTTG^-$ isotactic triad conformation.

(Keywords: PVC degradation; labile conformations; initiation mechanism)

INTRODUCTION

The degradation of poly(vinyl chloride) (PVC), one of the most widely used commercial polymers, is highly significant industrially, which accounts for the huge amount of research work performed over the last few decades. Yet, this crucial process, along with the stabilization of the polymers, remains to be understood, doubtless because research in this field has progressed in short, and often divergent steps. Owing to this fact, the mechanisms of the two basic steps involved in the degradation, namely initiation through labile structures and the propagation or build-up of polyenes, continue to attract the attention of polymer scientists.

Most authors agree that initiation is due to the presence of a few abnormal structures, i.e. allylic and tertiary chlorines, terminal insaturation, β-chloroallyl groups, etc.[1–11].

In contrast, in earlier work, we showed that the labile chlorine atoms are located at certain normal local chain conformations, in particular the isotactic triad $GTTG^-$, and that the length of polyenes resulting from the propagation step is related to the tactic sequence distribution. In effect, the longer the tactic sequence,

whether isotactic or syndiotactic, the longer the average polyene length in the degraded polymer. Polymers having no tactic sequences were shown to degrade at a much lower rate and to exhibit very short polyenes exclusively[12–15]. On the basis of these results, the thermal degradation of PVC may be thought to consist of two distinct processes. The first is an easy initiation through the labile chlorines at isotactic $GTTG^-$ conformations and a favoured propagation to give medium or long polyenes; the other consists of random initiation at the stable chlorines throughout the heterotactic parts of the chain and gives rise to short polyenes. For syndiotactic polymers, both difficult initiation and favoured propagation processes may be invoked[15]. This case, which is of less practical interest, is not considered in the present work in which only Bernoullian or tendentially syndiotactic samples are studied.

The fact that the two degradation processes mentioned above really occur has been given recent evidence through a kinetic study at temperatures ranging from 110 to 190°C for polymers of different tacticity, i.e. with different content of $GTTG^-$ conformation. It was actually demonstrated, on the one hand, that there are two processes with very different activation energies and polyene length in the polymer after degradation and, on the other hand, that their respective contributions to the

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overall degradation depend upon the content of *GTTG⁻* potentially existing in the polymers[16].

It must be pointed out that the changes in the content of *GTTG⁻* conformation in the polymers used in our research work originate either from the polymerization conditions, in particular the temperature, or from the removal of those conformations by stereospecific S_N2 nucleophilic substitution reaction, as studied extensively elsewhere[15,17].

The superiority of *GTTG⁻* isotactic triad conformation relative to other abnormal structures in initiating the thermal degradation of PVC, as inferred from our work, has been accepted by a majority of authors in this area[5,7,9,11], but it has been challenged by a few of them. Rogestedt and Hjertberg[18] have argued strongly that the contents of both the abnormal labile structures, namely allylic and tertiary chlorines, and the ordinary isotactic triad change with the polymerization temperature in parallel ways, so that the correlation between isotactic content and thermal instability of PVC, as found in our prior work, would in fact be relevant to allylic and tertiary chlorines. It should be noted, however, that in their attempt to compare the influence of tacticity and of labile defects on the degradation rate, these authors used four commercial polymers with overall isotactic triad fractions between 0.173 and 0.191, which correspond to contents of *GTTG⁻* non-defect labile structures of between 0.43 and 0.57% (ref. 19). In contrast, polymers with triad isotactic fractions between 0.12 and 0.22, that is with *GTTG⁻* content between approximately 0.10 and 0.80, have been investigated in our work, where the degradation rate was found to pass through a minimum at an isotactic fraction of around 0.16 (about 0.4% of *GTTG⁻*)[19].

On the other hand, the content of tertiary chlorine and of internal double bonds in the polymers used by Rogestedt and Hjertberg range from 0.07 to 0.2% and from 0.005 to 0.015%, respectively. Thus, the total content of abnormal labile chlorines lies between 0.075 and 0.21%. Consequently, there are few labile chlorines in the samples and their actual concentrations are less than half those of *GTTG⁻* non-defect labile structures. Based on these data and on our experience, we consider it quite hazardous to discard or to minimize the role of the *GTTG⁻* isotactic triad in PVC thermal degradation, as do Rogestedt and Hjertberg. Furthermore, they have overlooked two important approaches to this problem that arise from our work on S_N2 substitution reactions on PVC. One is that the thermal stability of the substituted polymers proves to be higher as the substitution extent increases up to a definite value, no higher than 1%, which depends on the fraction of isotactic triad in the starting material[13]. The other is that during the early stage of the reaction in cyclohexanone (CH), the only species to be removed are isotactic[20].

The above discrepancies in the nature of the labile chlorines in PVC prompted us to undertake new research in this field. This includes the thermal degradation of PVC after nucleophilic substitution in a number of solvents, which, as demonstrated recently[21], permits the removal of isotactic triads that are more likely to adopt the *GTTG⁻* conformation, with distinct degrees of selectivity. Secondly, it appeared of great interest to study the degradation of PVC samples after removing, at

least partly, the *GTTG⁻* conformation by exchanging it for the more stable *GTGT* conformation by means of physical processes where no changes in the content of allylic or tertiary chlorines can occur. This includes complexing the *GTTG⁻* conformations through specific interaction with compatible additives or polymers[22]; the stretching of films at temperatures near the glass transition temperature (T_g) so as to provoke *GTTG⁻ TT ⇒ GTGTTT* irreversible conformational change at *mmr* sequences[23]; and finally, annealing at temperatures ranging from 70 to 150°C in order to first induce the above conformational change and then, when raising the temperature over a certain threshold, to cause this change to reverse, thereby generating *GTTG⁻* conformations again as long as there are *mmr* sequences in the polymer. By doing that, we have endeavoured to give further evidence for the lability of *GTTG⁻* triad conformation and to respond to the well-known question regarding the fact that the thermal degradation of PVC continues steadily after the disappearance of the abnormal labile structures[24], which requires initiation by ordinary structures.

This paper deals in a comprehensive way with the results obtained in all the above research actions.

EXPERIMENTAL

Materials

Samples A, B and D were prepared by bulk polymerization at 90, 75 and 60°C, respectively, using 2,2′-azodiisobutyronitrile as initiator. Samples E, F, G and I were prepared by the same method but using u.v. irradiation to initiate polymerization at 40, 20, 0 and −50°C, respectively. Sample C was an additive-free commercial PVC prepared in bulk at 70°C; the process was stopped at conversion of 62%. Sample H was obtained in bulk at −30°C and corresponds to one of the samples studied in the IUPAC Working Party[10].

The number-average molecular weight was determined at 34°C in CH using a Knauer membrane osomometer. The solvents used were CH, tetrahydrofuran (THF), methyl ethyl ketone (MEK), *N*-methyl-2-pyrrolidone (MP), *N,N*-dimethylformamide (DMF) and hexamethylphosphoric triamide (HMPT); they were purified as described elsewhere[21]. Dioctylphthalate (DOP) and butyl stearate (BuSt) (Merck), poly(ethylene adipate) (PEA) and poly(ε-caprolactone) (PCL) (Aldrich) and polyarylate (a copolyester of bisphenol A with an equimolar mixture of isophthalic and terephthalic acids (PAr)) (Solvay & Cie) were used as received. Sodium benzenethiolate (NaBt) was prepared by the reaction of sodium (Merck) with thiophenol (Merck) as already described[20,21].

Substitution reaction with NaBT

Substitution reactions with NaBT at 25°C in various solvents were performed according to the experimental conditions described previously[21]. Another set of experiments was carried out in aqueous suspension at 60°C using tetra-n-butylammonium bromide (TBAB) and tetra-n-butylphosphonium bromide (TBPB) as phase-transfer catalysts following the method described in a previous paper[25]. The degree of substitution was determined by means of u.v. spectroscopy[19-21].

^{13}C n.m.r. spectroscopy

The tacticities of both the starting (samples A to E) and the modified polymers were measured by means of ^{13}C nuclear magnetic resonance (n.m.r.) decoupled spectra obtained at 85°C on an XL-300 Varian instrument, operating at 75.5 MHz using 1,4-dioxane-d_8 as solvent under conditions described previously[20]. The tacticities of samples F to I were measured in a 10% (w/v) solution in a mixture of deuterated dimethyl sulfoxide/1,2-dichlorobenzene (volume ratio 1/4) at 95°C. The resonances used were those of methine carbons of the backbone ranging from 57 to 61 ppm. In all the experiments 20 000–30 000 scans gave a very satisfactory signal-to-noise ratio and the respective peak intensities were measured from the integrated peak areas, as calculated by means of an electronic integrator.

Stretching polymers

Rectangular strips with dimensions 2 cm × 3 cm and thickness $100 \pm 5 \mu m$ were uniaxially drawn in an Instron dynamometer at $0.1 \, cm \, min^{-1}$. The samples were stretched at $90 \pm 1°C$ after previous conditioning in a thermostatic chamber. They were quenched in ambient air under tension.

I.r. measurements

A series of i.r. spectra of PVC pellets were recorded at temperatures between 60 and 150°C in a Nicolet 520 Fourier transform infra-red (FTi.r.) spectrometer. Thirty-two scans were signal-averaged at a resolution of $2 \, cm^{-1}$. The pellet was placed inside the temperature cell and kept for 30 min at the measuring temperature, after which a spectrum was recorded. The pellet was then quenched in liquid nitrogen and immediately another spectrum was recorded. A third spectrum of the sample was obtained after keeping the pellet at room temperature for 24 h. A pellet was prepared for each studied temperature. In order to obtain absolute measures of intensity changes with temperature, we recorded another series of spectra at temperatures between 80 and 150°C using the same pellet.

Thermal degradation

The samples were degraded to 0.3% in the solid state powder or film at 180°C using a thermostat with a silicone heating liquid. The HCl evolved during the experiments was swept out by means of a nitrogen flow $(9 \, l \, h^{-1})$ and trapped in ultrapure water (Milli-Q reagent water system; Molsheim, France) in a conductimetric cell so that the degradation could be continuously followed. The electrical conductivity of the solution was measured using an electrode cell connected to a Radiometer Copenhagen CDM 83 conductometer with automatic correction for temperature variations. The plots of evolved HCl against time are straight lines after an initial period. A more detailed description of this method has been published elsewhere[16].

U.v.–visible spectroscopy

U.v.–visible absorption spectra of degraded samples were measured with $4 \, g \, l^{-1}$ solutions in HMPT. They were recorded on a Perkin-Elmer 554 spectrometer at room temperature.

RESULTS AND DISCUSSION

Degradation of polymers after nucleophilic substitution to short conversions

The S_N2 nucleophilic substitution reaction on PVC has been studied extensively[19–21,25–28]. Basically, the reaction is stereoselective in that the only reactive species are *mmr* and *rrmr* sequences, that is the *mmm* isotactic triad and the *rm* heterotactic triad which are located at the end of isotactic or syndiotactic sequences, respectively. Moreover, in order for these structures to react, their respective conformations must be $GTTG^-TT$ and $TGTTTTT$. Otherwise, the requirements for the S_N2 mechanism are not fulfilled[26]. These conformations may exist in the polymer as the result of polymerization or they may be adopted during the substitution process. This is particularly important for *mmr*, which is known to show originally very low concentration of $GTTG^-TT$ conformation relative to the $GTGTTT$ conformation. Owing to the much higher reactivity of *mmr* on condition that it is under $GTTG^-TT$ conformation, its contribution to the whole substitution reaction will depend on both the fraction of *mmr* taking $GTTG^-TT$ conformation and the extent to which the remaining *mmr* can undergo the unlikely $GTGTTT \Rightarrow GTTG^-TT$ conformational change. As persistently shown, the latter factor depends in turn on the occurrence of specific, strong interactions between $GTTG^-TT$ conformation and the chemicals present in the reaction medium, such as solvents or additives[22].

The implication for the purpose of the present work is that for any given extent of substitution the amount of *mmr* structures that have disappeared can be regulated experimentally, which makes it feasible to study the effect of those structures on any property of the polymer. Examples for T_g and for antiplasticization processes have recently been published[21,29].

As illustrated by *Figure 1*, the S_N2 substitution reaction on the last *mm* triad of an isotactic sequence brings about the removal of either one $GTTG^-$ conformation or one $GTGT$ conformation by exchanging it for one $TTTT$ conformation. Because the $GTTG^-$ conformation is the actual reactive species, it appears reasonable to assume, in principle, that the first *mmr* structures to react are those under $GTTG^-TT$ conformation in the starting material.

Figure 2 depicts the early stage of substitution reaction with NaBT, in distinct types of solvent and in aqueous suspension in the presence of phase-transfer catalysts (PTC). Detailed studies have been published elsewhere[21,25]. Two important features are worth emphasizing: first, the slopes prove to depend on the reaction medium. Owing to the fact that *mmr* and *rrmr* are the only species to react[21], the slope is a good measure of the relative amounts of these structures that have disappeared at any conversion. Since all the slopes are higher than 0.5 it follows that *mmr* is preferred, although to a different extent, in every case. Secondly, the slope is unambiguously unity when the nucleophilic displacement of chlorine is made in CH or MEK at 5°C and 25°C. Thus none of the structures in PVC, other than *mmr*, disappears under these conditions. In effect, if it proved otherwise for any structure, however scarce it is in the polymer, the corresponding slope in *Figure 2* would have to deviate from unity, in contrast to what actually happens.
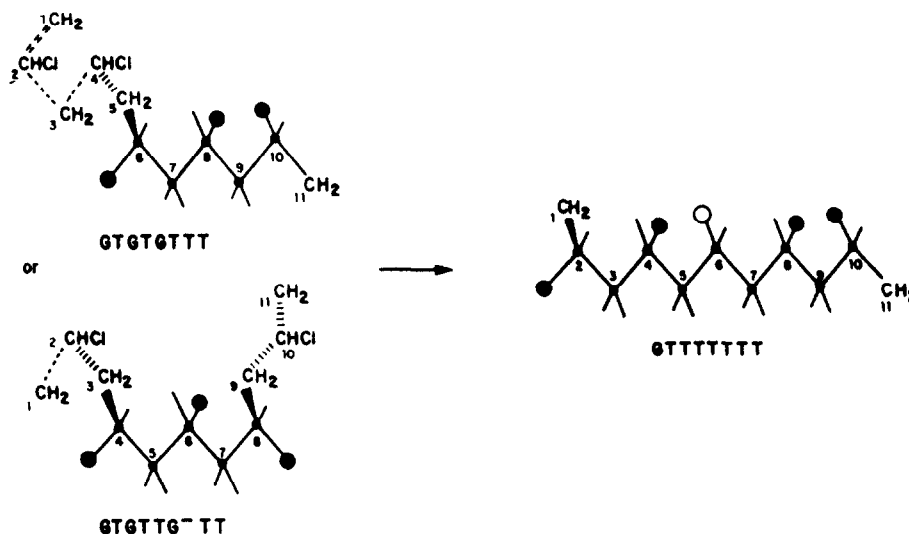
Figure 1 Conformational changes involved in substitution of PVC by the *mmr* pentad: ●, Cl group; ○, benzenethiolate group
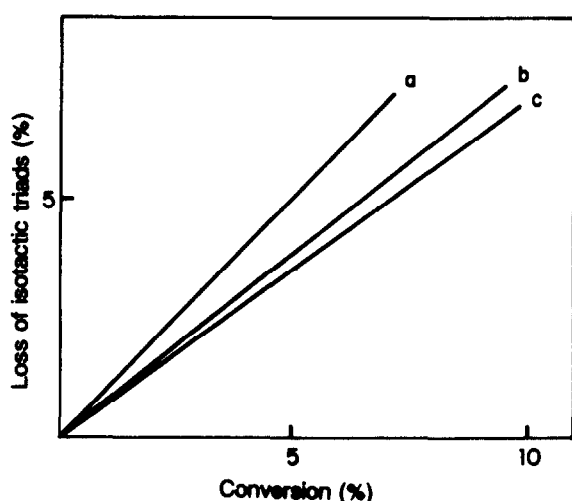

Figure 2 Evolution of microstructure with substitution (early stages) of PVC sample A. (a) CH, MEK[21]; (b) heterogeneous phase[25]; (c) MP, DMF[21]
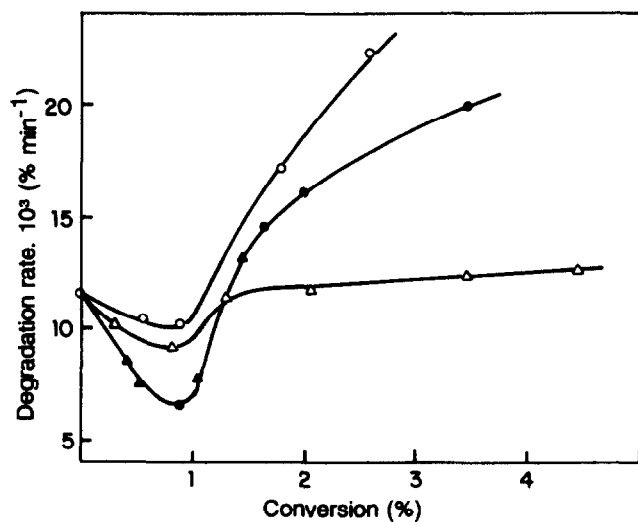

Figure 3 Degradation rate against substitution, sample A. CH: ▲, 5°C; ●, 25°C. △, Heterogeneous phase. ○, MP

The evolution of the degradation rate at 180°C with the substitution extent for the above three sets of modified polymers is displayed in *Figure 3*. As can be seen, the degradation rate passes through a minimum at a definite degree of substitution, which agrees with the content of $GTTG^-$ in the polymer (*Table 1*) for CH and MEK solvent, and tends to decrease for substitution in the heterogeneous phase and for MP and DMF solvents. It is notable that the degree of stabilization as the result of substitution decreases in the same order.

As shown in *Figure 4*, this stabilization is accompanied by a strong reduction of the content of long polyenes in the degraded polymer as compared with the undegraded sample.
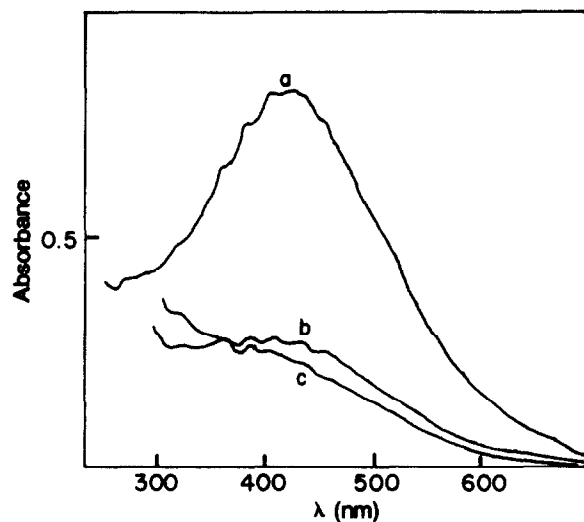
The results of *Figures 3* and *4* clearly indicate the observed stabilization to be due to the displacement of chlorines located at *mmr* structures. Actually, the higher the content of isotactic triad involved in the substitution reaction (*Figure 2*), the higher the degree of stabilization obtained.

This important conclusion is displayed in a quantitative manner by *Figure 5*. Very interestingly, the correlation between the percentage stabilization with respect to the starting polymer, as taken from the minima in *Figure 3*, and the extent to which the substitution involves *mmr* structures (α), as given by the slopes in *Figure 2*, is perfectly linear.

From the above correlations it follows that the labile structures that have been precluded at the minima of *Figure 3* are isotactic in nature, but no conclusion as the conformation of the *mmr* involved, whether $GTTG^- TT$ or $GTGTTT$, may be drawn. The occurrence of the minima of *Figure 3*, along with the fact that the loss of *mmr* is linear throughout the range of conversions considered (*Figure 2*), clearly indicates that those labile structures are only a fraction of the *mmr* existing in the polymer. Now, as shown in *Figure 1*, any substitution on *mmr* causes the content of all-*trans* syndiotactic sequences to increase. Indeed, it turns out that the polymer rapidly tends towards non-Bernoullian syndiotacticity when increasing the substitution extent[21,30]. This would account for the increase of degradation rate after the disappearance of the labile *mmr* structures. Since, as

Table 1 Data for the investigated polymers

Sample	t^a (°C)	M_n	^{13}C n.m.r.^{b}			h^c
			$P_{mm}{}^b$	$P_{mr}+P_{rm}{}^b$	$P_{rr}{}^b$	
A	90	21 500	0.215	0.504	0.281	0.77
B	75	23 400	0.198	0.508	0.294	0.62
C	70	44 000	0.200	0.497	0.303	0.64
D	60	39 300	0.196	0.493	0.311	0.63
E	40	78 200	1.170	0.499	0.331	0.40
F	20	81 000	0.156	0.510	0.334	0.25
G	0	97 800	0.154	0.468	0.378	0.24
H	−30	51 700	0.142	0.466	0.392	0.15
I	−50	48 000	0.119	0.477	0.404	–

^{a} Polymerization temperature
^{b} Probability of iso- (Pmm), hetero- (P_{mr}) and syndiotactic (P_{rr}) triads
^{c} Content of highly reactive structures in PVC as determined by substitution reaction with NaBT in CH at −30°C (ref. 19)

Figure 5 Degree of stabilization *versus* slopes of *Figure 2*

Figure 4 U.v.–visible spectra of modified samples after degradation (0.3%, 180°C). (a) Sample A; (b) MP 0.6%; (c) CH 0.9%
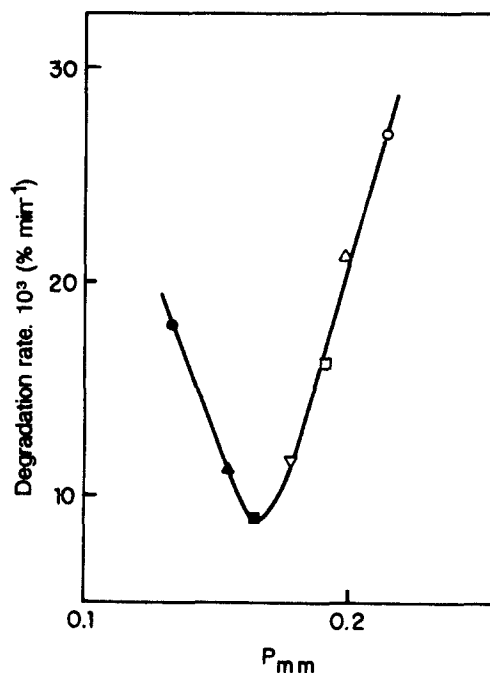
Figure 6 Degradation rate (180°C) *versus* isotactic content of PVC. Samples: A (○); B (△); D (□); E (▽); F (■); G (▲); I (●)

already argued, $GTTG^-TT$ is the highly reactive conformation of *mmr*, it appears quite reliable to attribute the lability of a fraction of *mmr*, as doubtless inferred from the above results, to the fact that they are taking the $GTTG^-TT$ conformation in the starting polymer.

Finally, it must be emphasized that these behaviours are quite similar in character to those observed by comparing the behaviour of polymers of different tacticities, as displayed by *Figure 6*[15].

Degradation of PVC in the presence of compatible agents

The purpose of this section is to verify whether or not the hindering of the *mmr* under $GTTG^-TT$ conformation, after complexing specifically with various compatible agents, involves improved stability in terms of both degradation rate and average length of the polyenes in the degraded polymers. That this specific complexing occurs has been demonstrated in very recent work. Indeed, it has been evidenced, through extensive *FT*i.r. spectroscopy investigations, that some carbonyl-containing products like CH, MEK and a number of esters, whether plasticizers or polyesters compatible with PVC, interact with the *mmr* structures and more specifically

with the fraction of them under $GTTG^-TT$ conformation[22].

Such interactions prove to be very strong, as clearly shown by two recent parallel findings in our laboratory: one is that solvents like CH and MEK are capable of displacing the conformational equilibrium $GTGTTT \rightleftharpoons GTTG^-TT$, which lies strongly on the side of $GTGTTT$ conformation, to the right side[21]; the other is that the presence of small amounts of plasticizer causes the β transition to decrease abruptly, as does the removal of a definite fraction of *mmr* through stereospecific nucleophilic substitution. This effect (antiplasticization) suggests that some local motions are hindered as the result of strong and specific interactions between some definite *mmr* structures and the plasticizer[29]. Based on these original results, we thought that such a restriction on
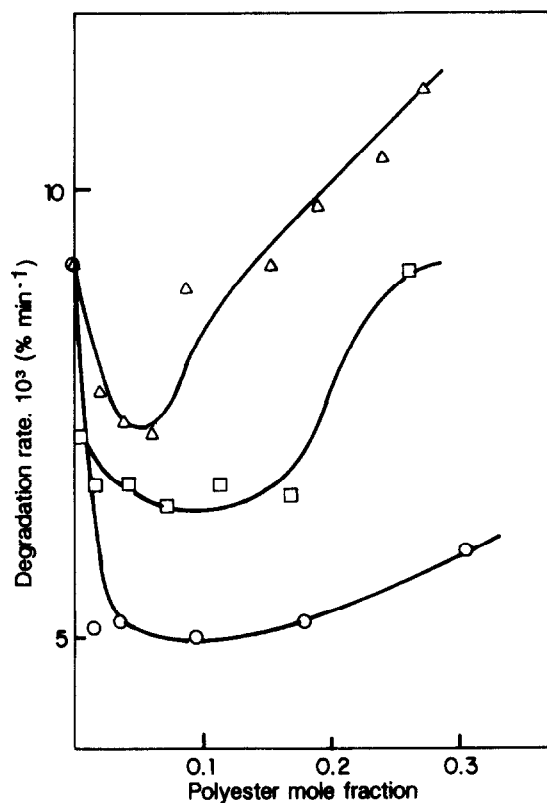
Figure 7 Degradation rate of PVC sample C/polyester blends *versus* composition. O, PVC/PCL; □, PVC/PAr; △, PVC/PEA

Figure 8 U.v.–visible spectra of various 0.3% degraded blends of PVC sample C/polyester (*Figure 7*) as compared to sample C (—). Polyester mole fraction: (a) (– – –) 0.02, (– · –) 0.06, (– –) 0.24; (b) (– – – –) 0.06, (– · –) 0.19, (– –) 0.36; (c) (– – – –) 0.05, (– · –) 0.17, (– –) 0.70

mobility of the labile *mmr* structure might prevent it from initiating the thermal degradation.

In *Figure 7* the degradation rate at 180°C of blends of sample C (*Table 1*) with three polyesters is plotted against the composition of the blends. From mere inspection it follows that the PVC blended with small quantities of polyester behaves similarly to the slightly substituted PVC (*Figure 3*) in that a substantial increase in stability occurs. Moreover, the order of stability improvement agrees with the degree of specific interaction between the respective polyesters and the *mmr* in PVC[31]. Correspondingly, the average length of the polyenes in the equally degraded polymers (*Figure 8*) decreases when the highest stability is attained, and this effect occurs in parallel ways to that of stabilization (*Figure 7*) or of interaction of polyesters with PVC[31].

The degradation process of the same PVC blends with two non-polymeric esters is illustrated by *Figures 9* and *10*. Here again, both a stabilization effect and a decrease in average length of polyenes is observed for small amounts of ester, even if these effects are less pronounced than in the case of polyesters, owing to either the higher interaction of DOP with structures of PVC other than *mmr* or the long aliphatic parts between the carbonyls in StBu, so restricting the probability of the specific interaction with *mmr*[22].

In our attempts to find evidence of the above correlations, we have compared the behaviours of PVC samples A, C and H of decreasing isotactic content (*Table 1*). The results are displayed in *Figures 11* and *12*, from which two important conclusions may be drawn. The first is that the stabilization is stronger and occurs at higher content of interaction agent as the isotactic content increases; the second is that no effect is observed for sample H, which happens to be tendentially
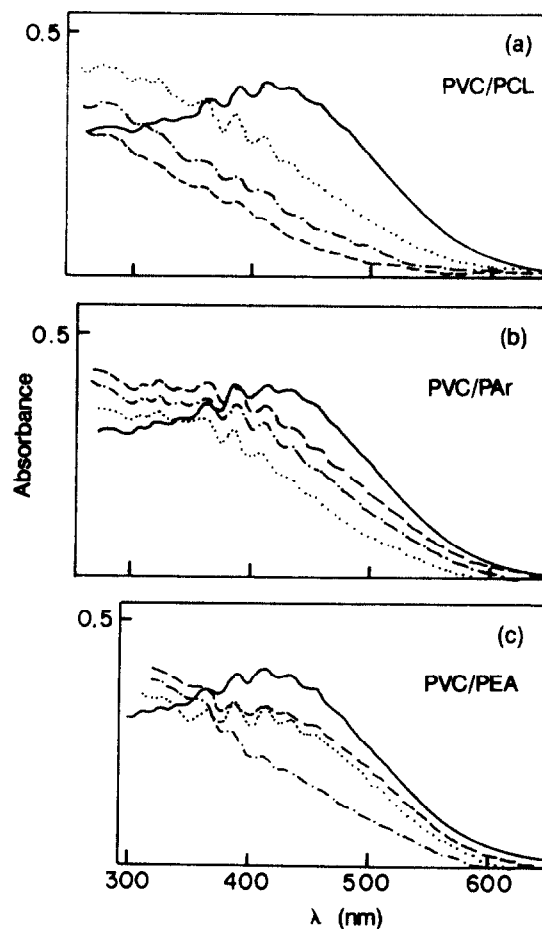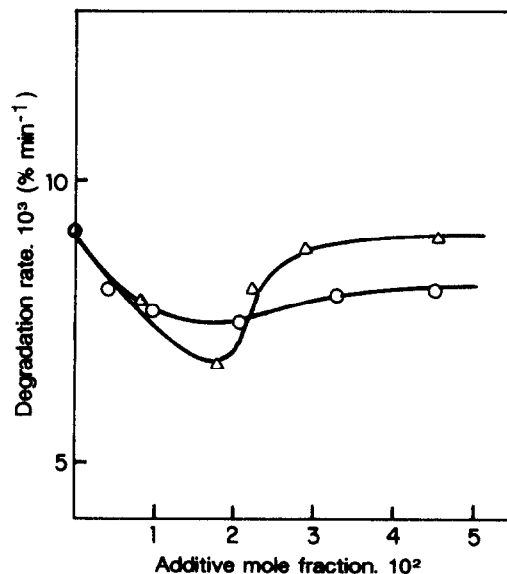

Figure 9 Degradation rate of additive blends *versus* composition. (△) PVC/DOP; (O) PVC/BuSt

syndiotactic so that its content of labile *mmr* should be negligible (*Table 1*). On the other hand, the evolution of the average length of polyenes (*Figure 12*) in the degraded polymers is consistent with expectations on the basis of the *mmr* content of each polymer, and with the evolution of degradation rates as shown by *Figure 11*.
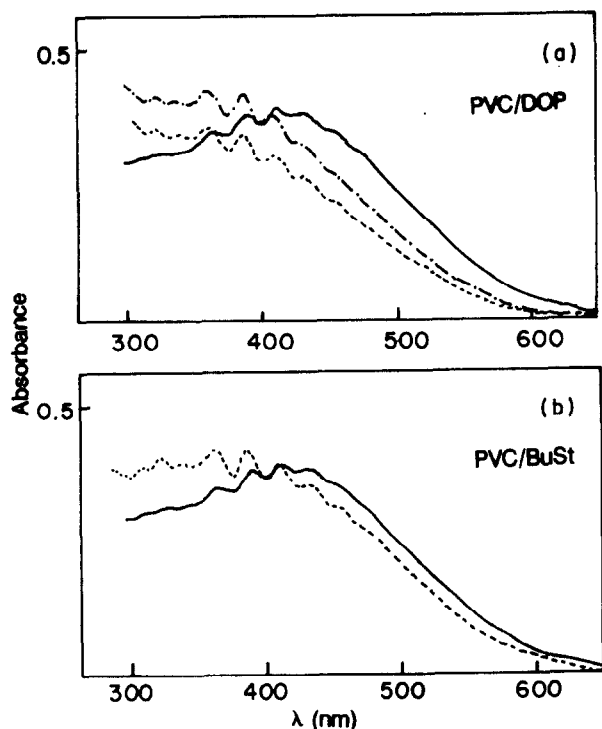
Figure 10 U.v–visible spectra of various 0.3% degraded PVC sample C/additive blends (*Figure 9*) as compared to sample C (——). Additive mole fraction: (a) (– – –) 0.008, (– · –) 0.02; (b) (- - - -) 0.02

Indeed, it should be noted that sample H exhibits no difference in polyene distribution in accordance with what happens to the degradation rate. The above results are further evidence that $GTTG^-$ isotactic triad conformation is the prevailing thermally labile structure in PVC.

Effects on thermal degradation

Elimination of labile conformations by stretching polymer films. It is well known that stretching a polymer film in one direction causes the polymer chains to tend to orientate themselves in the stretching direction. These orientation phenomena are usually investigated by *FT*i.r. dichroism. In general, the dichroic ratio $(A_{II}/A = R)$, between the absorption intensities for the polarization directions parallel and perpendicular to the stretching direction provides useful information as to the geometrical structure of the polymer chain.

The orientation is generally assumed to disappear when the temperature is raised above T_g so as to allow the polymer chains to be released from the constraints induced by the orientation and, consequently, to recover the initial state. In this respect, the possible occurrence of some irreversible conformational changes during stretching has been a persistent concern in our laboratory. Of all the conformational changes that are possible in PVC, the $GTTG^-TT \Rightarrow GTGTTT$ in the *mmr* sequence is the only one to involve a local lengthening of the chain. This is quite apparent from *Figure 13*.

As also illustrated by *Figure 13* and by a recent publication[32], the $GTTG^-$ conformation is of much higher potential energy than $GTGT$, which is consistent with both the higher local mobility and the weaker interchain interaction at the former conformation, as argued previously[21,23]. Thus, we thought it highly unlikely that the former conformation would be
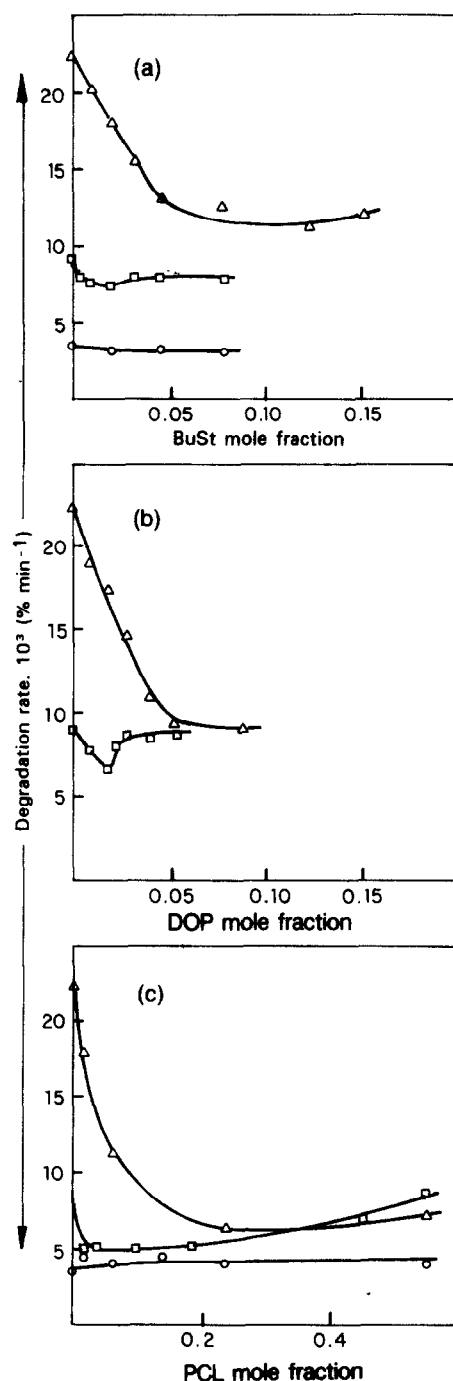

Figure 11 Degradation rate of PVC-based blends *versus* composition. (a) PVC/BuSt. (b) PVC/DOP. (c) PVC/PCL: △, sample A; □, sample C; ○, sample H

recovered after the disappearance of orientation, whether by heating at moderate temperatures or by solution of the films. In fact, temperatures as high as 130°C are needed to get the above conformational change slightly reversed (see following section).

Therefore, verifying that the $GTTG^-$ conformations in a PVC film disappear upon stretching and that they are not recovered upon annealing or dissolving the stretched films, would not only demonstrate the occurrence of irreversible conformational changes but could be of crucial interest in investigating the stability-determining role of that conformation, because no alteration of tertiary or allylic chlorines is to be expected from those physical treatments.
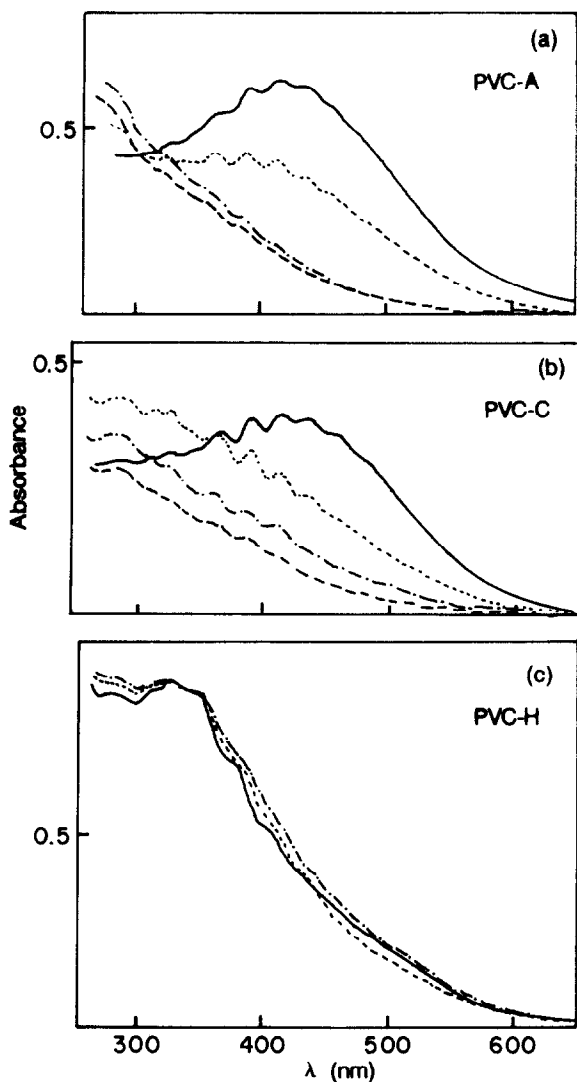
Figure 12 U.v.–visible spectra of various 0.3% degraded PVC-based blends (*Figure 11*) as compared to the respective PVC (———). Polymer mole fraction: (a) (- - - -) 0.06, (– · –) 0.24, (– –) 0.55; (b) (· · · · ·) 0.02, (– · –) 0.06, (– –) 0.24; (c) (· · · · ·) 0.06

chain conformations. Besides, each of these frequencies is thought to depend on the local environment in which the bands find themselves[22]. Thus the 637 cm^{-1} band has been assigned to S_{HH} flanked by two S_{HH} modes $(S_{HH}(S_{HH})_a S_{HH})$, while S_{HH} flanked by two S_{CH} $(S_{CH}(S_{HH})_b S_{HC})$ modes is responsible for the frequency at 622 cm^{-1}, which is usually overlapped by the absorption around 615 cm^{-1}. This latter frequency obeys S_{HH} modes flanked by one S_{CH} mode and one S_{HH} mode $(S_{CH} \cdot (S_{HH})_c S_{HH})$. We denote these frequencies $(S_{HH})_a$, $(S_{HH})_b$ and $(S_{HH})_c$, respectively. Interestingly, they are likely only in the $TTTT$ syndiotactic triad, the $GTTG^-$ isotactic triad and the $GTTT$ heterotactic triad, respectively[21,31].

Turning to *Figure 14* it appears quite clear that the band at 615 cm^{-1} increases with stretching in comparison with the band at 637 cm^{-1}. On the other hand, from the changes of dichroic ratio (R) with stretching (*Figure 15*) it follows that the 615 cm^{-1} and 637 cm^{-1} bands are of rather low and relatively high perpendicular nature, respectively. In principle, this seems reasonable because in the case of the ... $TTTT$ ... syndiotactic sequences all the C–Cl bonds are perpendicular to the chain axis. In contrast, the C–Cl bond of the S_{CH} chlorine in $GTTT$ heterotactic triad deviates markedly from the perpendicular position, as do the two S_{CH} chlorines in $GTTG^-$ isotactic triad (see *Figure 13* on the right and left sides, respectively). Still, the fact that the dichroic ratio for the 615 cm^{-1} band decreases up to an elongation of roughly 1.5 and then tends to stabilize, would also agree with the occurrence of conformational changes that might result in a higher number of C–Cl bonds perpendicular to the chain axis. This is the case of the change between the two conformations that are likely in *mmr* sequence (*Figure 13*). As can be seen, it involves the following change in C–Cl stretching vibration modes:

$$S_{CH} \cdot S_{CH}(S_{HH})_b \cdot S_{HC} S_{HH} \Rightarrow S_{CH} \cdot S_{CH} \cdot S_{CH}(S_{HH})_c \cdot S_{HH}$$

Two implications follow. (i) The short all-*trans* part in *mmr* is lengthened and two consecutive C–Cl bonds perpendicular to the chain axis appear, this ought to

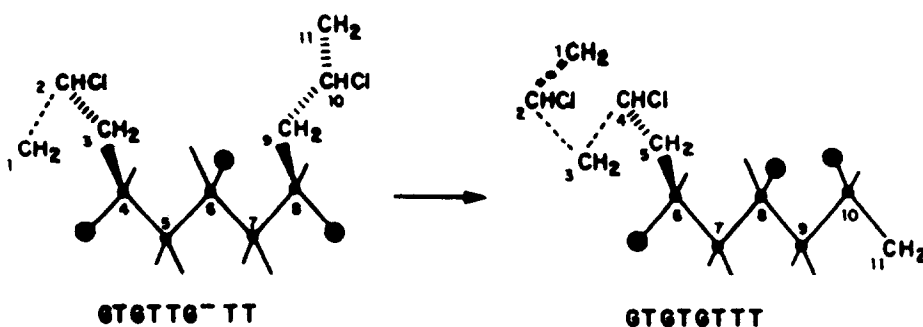GTGTTG⁻TT   GTGTGTTT

Figure 13

The evolution of the i.r. bands of C–Cl bond with degree of stretching (λ) is shown by *Figure 14A*. The assignment of these bands has been well documented[33,34]. As a whole, the bands at 695 cm^{-1} and 685 cm^{-1} are due to S_{HC} absorption modes, while the bands centred at 637 cm^{-1} and 615 cm^{-1} obey S_{HH} absorption modes of C–Cl bond. (The suffix refers to the *trans* substituents on both C–C bonds adjacent to the C–Cl bond.) These bands are therefore very sensitive to

result in a moderately enhanced absorption intensity of the 615 cm^{-1} band in the perpendicular direction. (ii) One $(S_{HH})_c$ chlorine is formed at the expense of one $(S_{HH})_b$ chlorine, thus, the disappearance of a shoulder at 622 cm^{-1} and an increase of the band at 615 cm^{-1} should be expected in the spectrum registered with non-polarized light.

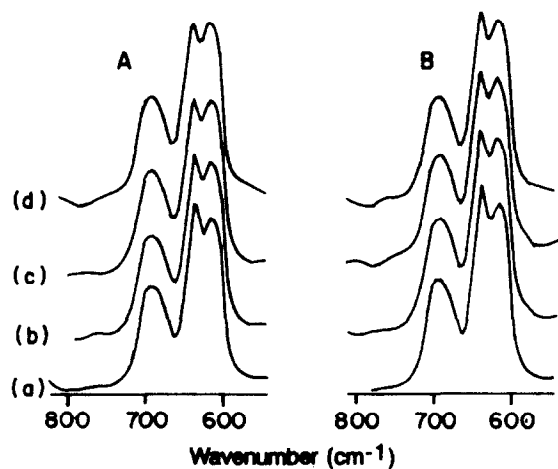The conclusion we come to is that the perpendicular dichroism shown by *Figure 15* originates from two

Figure 14 Changes in *FT*i.r. spectra with stretching (λ). Value of λ: (a) 1; (b) 1.3; (c) 1.5; (d) 1.9. (A) Stretched films and (B) recovered films of sample B
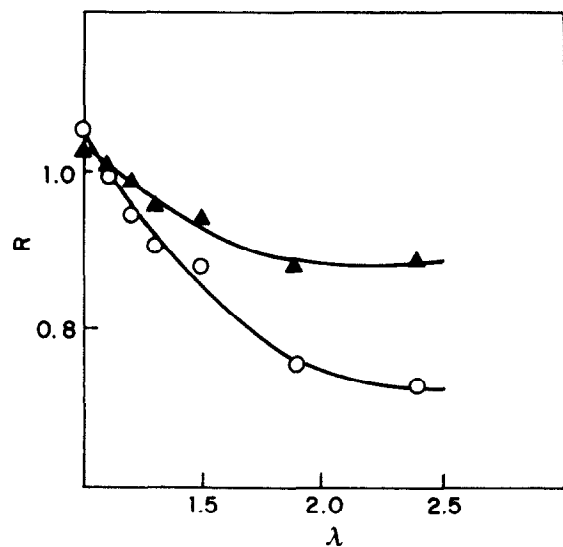

Figure 16 Relative absorbance of A_{615}/A_{637} (●) and $A_{615}\perp/A_{637}\perp$ (○) *versus* stretching

Figure 15 Dichroic ratio (*R*) of the bands at $615\,\text{cm}^{-1}$ (▲) and $637\,\text{cm}^{-1}$ (○) *versus* stretching
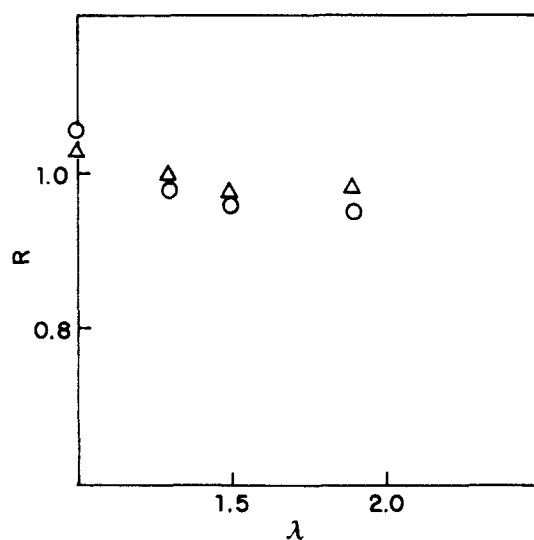
Figure 17 Dichroic ratio (*R*) of the bands at $615\,\text{cm}^{-1}$ (△) and $637\,\text{cm}^{-1}$ (○)

distinct processes: one is the conformational change in *mmr* and it should affect the $615\,\text{cm}^{-1}$ band; the other is the normal chain orientation that would be connected with the higher perpendicular behaviour of the band at $637\,\text{cm}^{-1}$.

As illustrated by *Figure 16* the experimental results account thoroughly for the above statements. Actually, when the relative absorbance A_{615}/A_{637}, as taken from the spectra registered without polarizer, is plotted against the degree of stretching it appears evident that at stretching degrees as short as 1.1–1.2 there is a rather abrupt increase of the band at $615\,\text{cm}^{-1}$ which then tends to vanish. This is quite consistent with the occurrence of the conformational change of *Figure 13*. On the other hand, similar plots with the absorption intensities at $615\,\text{cm}^{-1}$ and $637\,\text{cm}^{-1}$ in the perpendicular direction (*Figure 16*) show two well differentiated behaviours: during the first stage of stretching the perpendicular behaviour of the band at $615\,\text{cm}^{-1}$ strongly prevails over that of the $637\,\text{cm}^{-1}$ band, while the reverse occurs as the stretching surpasses the 1.5 value, because of the $GTTG^-TT$ conformation depletion through the conformational change of *Figure 13*.
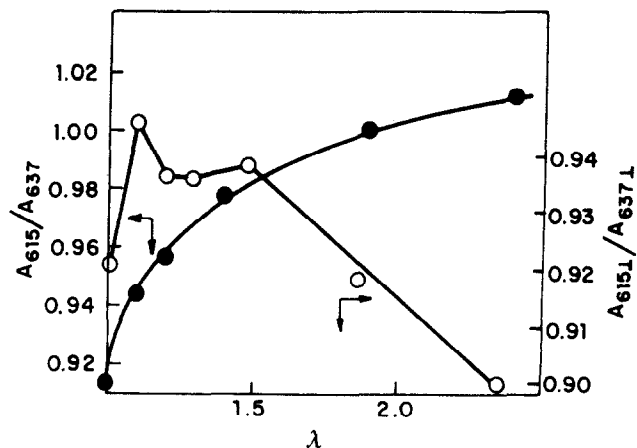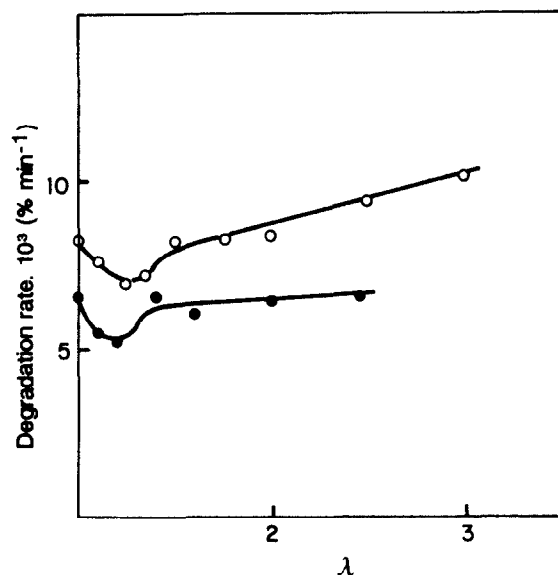

Figure 18 Influence of stretching on degradation rate for PVC sample B films (○) and the powders resulting from dissolving the same stretched films (●)
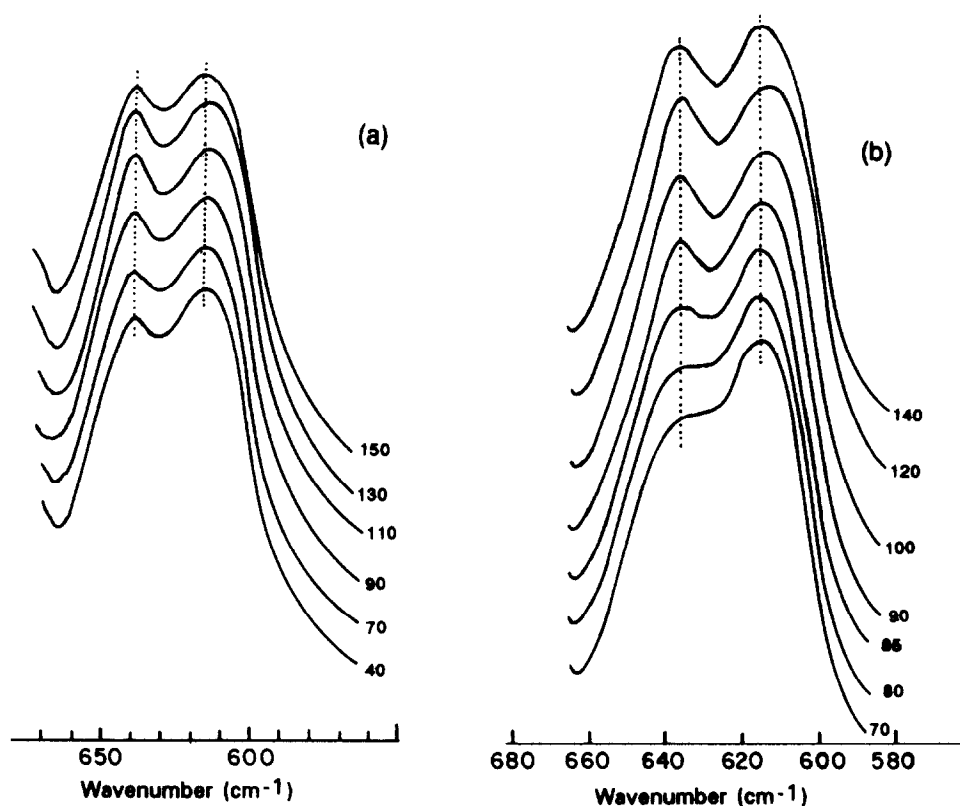
Figure 19 Changes in *FT*i.r. spectrum with temperature: (a) sample B; (b) sample A

Whether and to what extent the disappearance of the *GTTG⁻TT* conformation as the result of stretching is irreversible has been investigated by comparing the *FT*i.r. spectra of the stretched films with those of the same films after either annealing in boiling water for 20 min or dissolving in THF and then forming a film again by leaving the solvent to evaporate under vacuum at 40 °C. These series of films are denoted 1, 2 and 3, respectively.

As can be seen from *Figure 14B*, no appreciable changes in the relative intensities of the 615 cm⁻¹ and 637 cm⁻¹ bands are observed for the films of series 2, so accounting for the irreversibility of that conformational change. This is more interesting as the orientation has disappeared upon annealing of the films (*Figure 17*), so that the residual perpendicular behaviour of the 615 cm⁻¹ band should be due to the fact that no *GTTG⁻TT* conformations have been recovered.

If the conformational change of *Figure 13* is indeed irreversible, then it follows that the labile *GTTG⁻* conformations in the film prior to stretching must have disappeared in 1, 2 and 3 series of films. As a consequence, a stabilization effect upon short stretching (around 1.2–1.3) would be observed in all cases.

The evolution of the degradation rate with the degree of stretching both for series 1 and for the powders obtained by dissolving the stretched films (series 2) in the THF and precipitating with methanol is displayed by *Figure 18*. As can be seen, the stabilization agrees with degrees of stretching of 1.1–1.2, that is when *GTTG⁻* conformations have disappeared, which accounts for the lability of these conformations.

From these results it follows that once the conformational change of *Figure 13* has operated and, consequently, the *GTTG⁻* conformations have disappeared, the corresponding stabilization of the polymer remains

unaltered, irrespective of any subsequent physical treatment. This is more significant as the physical treatment may influence the overall degradation rate, in particular when the propagation step is affected, as is the case of orientation.

The above results are clearly at variance with the degradation mechanisms based on tertiary or allylic chlorines as the prevailing labile structures in PVC, and they give further evidence of the lability of the normal *GTTG⁻* conformation as proposed by our research work in this area.

Thermally induced elimination of labile conformations. An experiment aim to provoke changes in the content of *GTTG⁻* conformation by annealing at temperatures ranging from below T_g to levels high enough for the interchain interactions in the polymer to be released, has been made in our attempt to prove the lability of that conformation. Based on our early studies on tacticity dependence of thermal and photochemical degradation of PVC, we expected the permanent *GTTG⁻* conformations arising from polymerization to rotate into the more stable *GTGT* conformation when heating the polymer at temperatures near T_g. Conversely, at higher temperatures, where no strong intermolecular constraints exist, the population of less stable conformers like *GTTG⁻* ought to increase. Moreover, it was believed that both changes could very well take place at different parts of the polymer depending on the environment of the *mmr* conformation. Since no change in population of allylic or tertiary chlorines can result from these treatments, some new arguments in favour of the lability of *GTTG⁻* conformation might be afforded in this way.
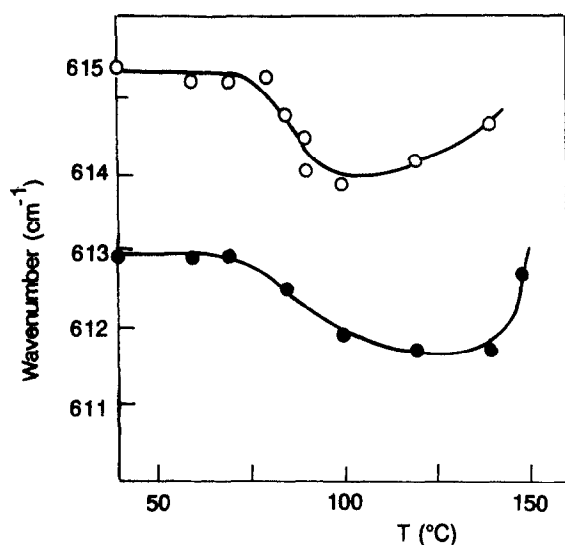
Bearing these ideas in mind, we designed two parallel

Figure 20 Shift of absorption around 615 cm^{-1} with temperature: ○, sample A; ●, sample B
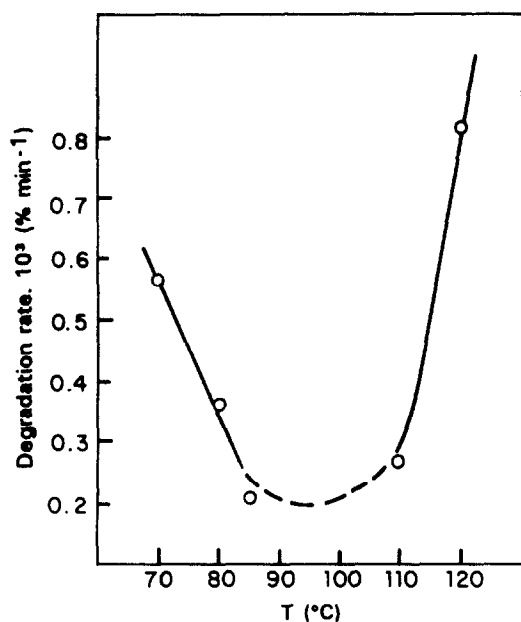

Figure 21 Variation of the initial degradation rate with annealing temperature of sample B

courses of action. The first consisted of recording the *FT*i.r. spectrum at temperatures between 80 and 150°C using a single KBr pellet. The other involved heating the individual KBr pellets to the same temperatures for 30 min followed by immediate quenching. Three *FT*i.r. spectra were registered for every pellet: (1) at the selected temperature; (2) just after quenching; and (3) after 24 h at room temperature. No appreciable difference between these spectra was found. The influence of the potential conformational changes on the initial degradation rate, as measured under the usual conditions in our laboratory, could thus be investigated.
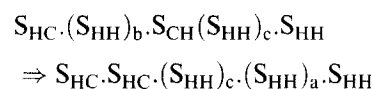
The evolution of the stretching vibration bands of C–Cl bond with temperature for PVC samples A and B of different tacticities (*Table 1*) is shown in *Figure 19*. Interestingly, the absorption around 615 cm^{-1} changes both in position and in width, and the shoulder at 622 cm^{-1} vanishes quickly. In contrast, only intensity

changes are observed for the band at 637 cm^{-1}. Note that the former change is particularly enhanced in sample A, with higher isotactic content.

From *Figure 20*, showing the shift of the highest absorption around 615 cm^{-1} *versus* temperature, it may be concluded that the band moves towards lower frequencies at temperatures between 80°C and 100–110°C; then it tends to move in the reverse order. Taking into account the three known contributions to that absorption, as studied extensively by several authors[33,34], these results clearly indicate that the relative average populations of the $GTTG^-$ isotactic triad conformation [$(S_{HH})_b$ mode absorption at 622 cm^{-1}], the $GTTT$ heterotactic triad [$(S_{HH})_c$ mode absorption at 615 cm^{-1}] and the $TTTT$ syndiotactic triad [$(S_{HH})_a$ mode absorption at both 637 and 602 cm^{-1}] are changing with temperature, in that up to 100–110°C the content of the third conformation increases at the expense of that of the first conformation. This is clearly supported by the fact that the band at 637 cm^{-1} increases without moving throughout the whole treatment. The shifts of *Figure 19* make it impossible to accurately measure the intensity of the 615 cm^{-1} band.

At temperatures higher than 110°C the band around 615 cm^{-1} is shown to shift in the reverse order and to narrow somewhat, in particular on the 604 cm^{-1} side. In this respect it is worth noting that the trend of the band at 635 cm^{-1} is towards a decrease in absorbance, but it never returns to the early state. The behaviour of this band has been studied in a much more detailed way by Koening and Antoon[35], who, however, did not consider the band at 615 cm^{-1}.

In the light of the known assignment of the conformationally sensitive bands of C–Cl bond in PVC (see preceding section and references cited therein), the results of *Figures 19* and *20* would account for the conformational change of *Figure 13* to occur in *mmrrr* sequences up to 100–110°C as follows:

$$S_{HC} \cdot (S_{HH})_b \cdot S_{CH} (S_{HH})_c \cdot S_{HH}$$

$$\Rightarrow S_{HC} \cdot S_{HC} \cdot (S_{HH})_c \cdot (S_{HH})_a \cdot S_{HH}$$

As a result, both the disappearance of the shoulder at 622 cm^{-1} and the increase of the bands at 637 and 604 cm^{-1}, would have to occur, as actually happens. Note that, as argued in the preceding section, the same conformational change at *mmrrm* sequences affects the 622 and 615 cm^{-1} bands but not the 637 cm^{-1} band.

As to the behaviour at temperatures higher than 110°C (*Figure 20*), it is apparent from the evolution of spectra (*Figure 19*) that the above conformational change is reversed, thereby allowing some $GTTG^-$ conformations to appear again. Nevertheless, the fact that there is little decrease of the band at 637 cm^{-1}, even at temperatures as high as 150°C, leads one to think that this change could very well take place by sequences other than *mmrrr*. Be that as it may, the occurrence of two competing effects, implying depletion or formation of $GTTG^-$ conformations depending on the temperature, ought to be assumed on the basis of the above results. Interestingly, the second effect accounts for the continuous appearance of $GTTG^-$ labile sites during the overall degradation process as long as there are *mmr* configurations in the polymer. As often argued[5,7,24], this has been an important problem to solve for the mechanism of

thermal PVC degradation to be clarified. *Figure 21* presents the initial degradation rate at 180°C as a function of the annealing temperature. As can be seen, the trend of degradation rate is towards a stabilization up to annealing temperatures between 80 and 110°C and towards a decrease in stability at higher temperatures. This is consistent with the changes in availability of *GTTG* conformations as shown by the above *FT*i.r. results.

This behaviour provides conclusive support for our proposal that the initiation of thermal degradation in PVC is due, to the greatest extent, to the occurrence of *GTTG⁻* conformation either during the polymerization or during the degradation process as a result of thermally induced conformational changes.

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