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G. Martínez[a]; C. Mijangos[a]; J. Millán[a]
[a] C.S.I.C. Instituto de Plásticos y Caucho, Madrid, Spain

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Selective Substitution Reactions on PVC. Lability of Some "Normal" Structures

G. MARTÍNEZ, C. MIJANGOS, and J. MILLÁN

C.S.I.C. Instituto de Plásticos y Caucho
Madrid 6, Spain

ABSTRACT

The nucleophilic substitution reaction on PVC with sodium thiophenate in cyclohexanone solution is studied. The reaction appears to be S_N2 substitution and it involves three different steps with decreasing reaction constants. By using ^{13}C-NMR spectroscopy, the fast step is proposed to be due to the high reactivity of the central chlorine in isotactic triads and, to a lesser extent, in heterotactic triads. The study of the thermal degradation of the modified samples shows that during the fast step of substitution a stabilizing effect occurs, and that as soon as the first step is over, the polymer stability decreases markedly. These effects are accompanied by changes in polyene distribution as proved by UV-VIS absorption spectroscopy study on degraded samples. The results, as discussed on the basis of the possible conformations of triads in PVC, suggest that some chlorine atoms in both the GTTG isotactic and the TTTG heterotactic triads should be considered as labile structures in PVC. It follows from the results obtained that on the one hand the initiation of degradation may occur by normal structures, and on the other the build-up of polyenes is favored by the presence of ...TTTT... sequences. Both features contributing to a better understanding of the degradation of PVC.

INTRODUCTION

Much research on poly(vinyl chloride) (PVC) thermal degradation has been carried out in the past. Many publications in this field have been surveyed in some recent reviews [1-4]. According to most workers, the nonoxidative degradation of PVC starts from polymer defect sites such as allylic chlorine, tertiary chlorine, oxygen-containing groups, branches, and head-to-head structures [1] which are usually referred as "abnormal" structures in PVC. Nevertheless, a quantitative correlation between "abnormal" structures content and PVC stability has not been reported so far, probably because of the difficulties found in the quantitative estimation of these structures. This circumstance, besides the fact that the "abnormal" structures content in PVC appears to be low, make it doubtful to consider that the "abnormal" structures are the exclusive cause of instability in PVC.

On the other hand, even if the possibility of initiation of degradation through "normal" structures is now receiving increasing attention [4], no work on this subject has been published so far.

We have found [5-9] that the tacticity distribution in PVC has a marked influence on the thermal degradation mechanism. We demonstrated that tactic sequences, isotactic or syndiotactic, favor the ready propagation of the unzipping reaction involving the sequential loss of hydrogen chloride, because the relative proportion of longer polyene sequences is higher the greater the tactic sequence content of either type. This effect is much more pronounced for syndiotactic polymers [5-7]. Polymers which do not have pronounced tactic sequences because the polymerization process obeys Bernoullian propagation statistics, have a higher degree of thermal stability and a relatively low content of longer polyene sequences after degradation.

Although the above results concern the propagation of degradation, it is worth noticing that the lower stability of non-Bernoullian and favored isotactic-placement containing polymers was found to be accompanied by a higher number of initiation sites relative to syndiotactic non-Bernoullian polymers [9]; this clearly suggests the occurrence of a higher labile structures content in the former polymers. It is therefore very interesting to know whether the above labile structures are "normal" conformations of isotactic placements or not. This is the purpose of the present work.

Among the possible conformations in PVC, whether they be isotactic or syndiotactic [10], we believed that the central carbon atoms in the isotactic GTTG triad and the heterotactic TTTG triad are, in principle, much more reactive in nucleophilic substitution than the others because both the nucleophilic attack and the chlorine atom separation are sterically more favored. Therefore we undertook the study of the reaction of PVC with sodium thiophenate as the nucleophilic agent in order to investigate the effect of the possibly selective substitution on the thermal stability. This reaction seemed to be all the more enlightening because the chlorine atoms in the above quoted "abnormal" structures do not satisfy the steric conditions for nucleophilic substitution.

In this publication we report our preliminary results concerning some kinetic features and the selectivity of the reaction on the one hand, and the lability of chlorine atoms in some of the "normal" conformations in PVC on the other.

EXPERIMENTAL

Polymer Preparation

The PVC sample used was prepared at 60°C in bulk using 2,2'-azobisisobutyronitrile (AIBN) as the initiator system. The full details have been published [8]. The 60° C dioxane soluble fraction of the whole polymer was used. The average molecular weight, as determined by viscometric measurements of the whole polymer, was about 50,000 [8].

Substitution Reaction with Sodium Thiophenate

The sodium thiophenate was prepared by reaction of purified sodium with thiophenol in p-xylene and under an inert atmosphere. The reactor was heated moderately to make sure the p-xylene refluxed during the entire reaction. The precipitate was filtered under an inert atmosphere and then dried under vacuum.

For the substitution reaction, 24 h prior to the experiment, the appropriate amount of C_6H_5SNa was dissolved in a part of the purified cyclohexanone used. The polymer was dissolved in the other part of the solvent. Both solutions, independently thermostated at -15°C, were poured into the reaction vessle which was also thermostated at -15°C by means of a stream of methanol from the ultracryostat. All the experiments were carried out under an inert atmosphere. At appropriate reaction times, samples were drawn out and at once precipitated with methanol, then they were washed with methanol and with heptane, and dried at 40°C under vacuum.

The reaction conditions for the three sets of experiments used in this work are given in Table 1. In the case of Reaction A, a slight turbidity as well as a considerable viscosity in the reaction medium were observed because the reactant concentrations used are high. Since no changes in the reaction kinetics or in the behavior of polymers were noted, these anomalies were overlooked.

All the samples were characterized by IR and UV-VIS spectroscopy. Although the IR bands of incorporated thiophenate are observable from conversions between 0.5 and 1%, they are overlapped by

TABLE 1. Substitution Conditions for Reactions A, B, and C (Fig. 2) and Rate Constant Values (Fig. 3)

Reaction	Mol/L PVC $\times 10^2$	Mol/L C_6H_5SNa $\times 10^2$	Rate const $\times 10^2$ (L/mol·min)		
			k_1	k_2	k_3
A	6.4	7.6	25	1.5	0.3
B	6.4	5.1	25	1.5	0.4
C	3.2	5.1	25	1.4	0.4

those of unmodifed PVC, which makes them of no use for kinetic measurements. Conversely, a new band centered at about 256 nm in the UV-VIS spectra is observable at much lower conversions and makes it possible for the kinetics to be followed on condition that a good calibration curve is available (see spectra in Fig. 1). This was the case in the present study where the calibration curve was obtained with known solutions of butyl mercaptane in tetrahydrofuran. The modification extents so obtained were in very good agreement with those obtained through the chlorine content analysis.

The conversion curves for the reactions in Table 1 are plotted in Fig. 2, and the corresponding values for Reaction A are given in Table 2 where the underlined samples were used for comparison purposes in this work.

The reaction appears to be second order. Accordingly, the reaction rate will be given by

$$v = dx/dt = k(a - x)(b - x)$$

where k is the reaction rate constant, a is the initial concentration of PVC, b is the initial concentration of the nucleophile, and x is the concentration of modified units.

By integrating the above expression, one gets

$$\log \frac{1 - \alpha}{1 - \beta} = \frac{(a - b)kt}{2.303}$$

where $\alpha = x/a$ and $\beta = x/b$ represent, respectively, the PVC fraction and the nucleophile fraction reacted at a certain time t.

The plots of $\log (1 - \alpha)/(1 - \beta)$ as a function of time, t, for Reactions A, B, and C are given in Fig. 3. The values obtained for the three reaction constants from the slopes in Fig. 3 are included in Table 1.

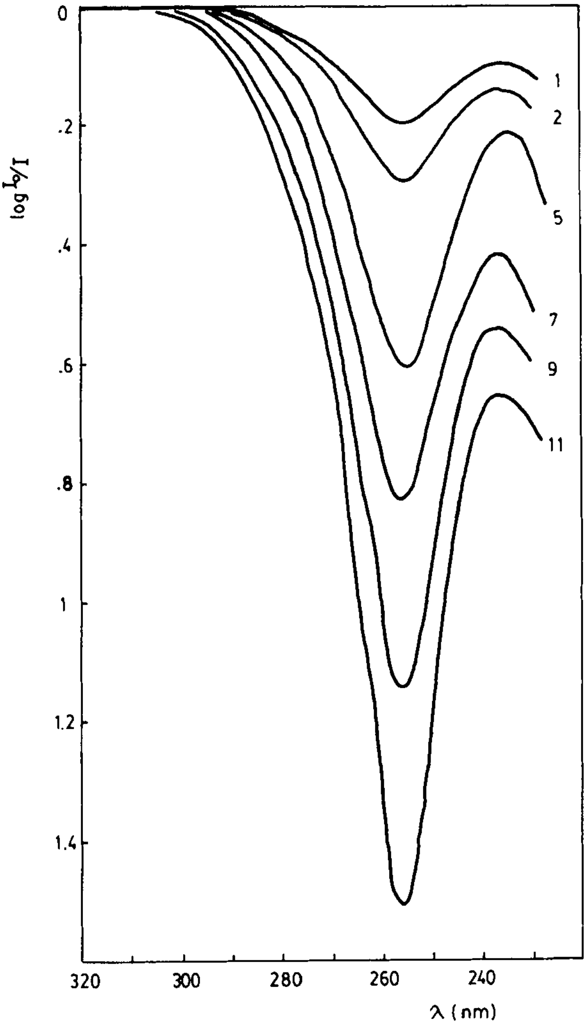

FIG. 1. UV spectra of modified samples from Reaction A (see Tables 1 and 2).

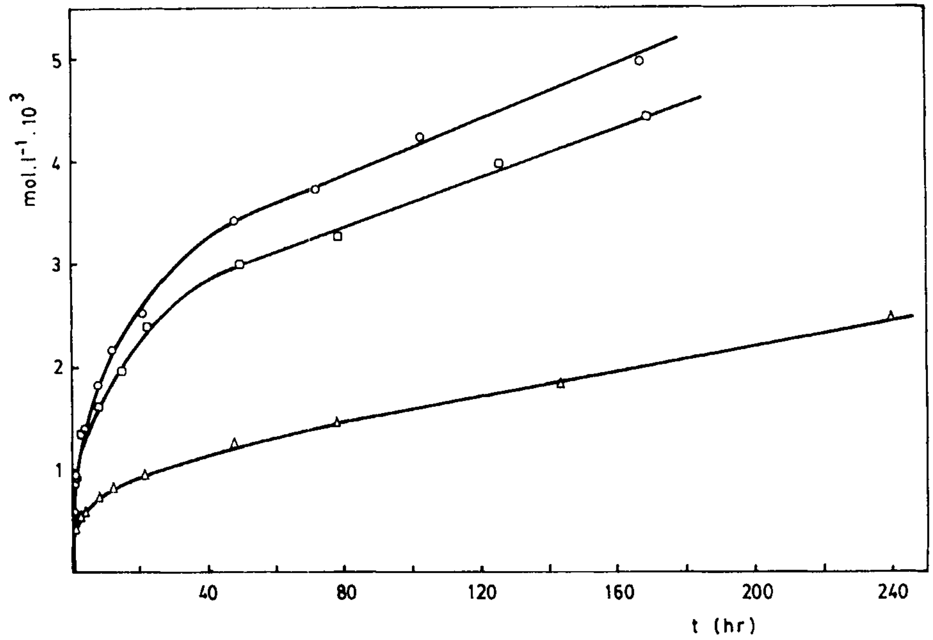

FIG. 2. Nucleophilic substitution on PVC with sodium thiophenate: (○) Reaction A, (□) Reaction B, (△) Reaction C (see Table 1).

Ultraviolet Visible Absorption Spectroscopy

UV-VIS absorption spectra of the modified samples were measured in solutions of 0.8 g/L in tetrahydrofuran. They were examined with a Varian Techtron 635 spectrometer at room temperature, using a 0.8 g/L solution of unmodified PVC in tetrahydrofuran as reference (Fig. 1).

UV-VIS absorption spectra of degraded samples were measured with solutions of 1.7 g/L in hexamethylphosphoric triamide. They were registered on a Perkin-Elmer 554 spectrometer at 40°C in an inert atmosphere. 1.7 g/L solutions of the corresponding undegraded polymers were used as a reference.

^{13}C-NMR Spectroscopy

Fourier transform ^{13}C-NMR spectra were recorded using an external locked field (hexadeuterated dimethylsulfoxide, DMSO) at 25.2 MHz with a Varian XL-FT-100 spectrometer. Proton noise decoupling was employed. The spectra were obtained at 130°C using

TABLE 2. Detailed Data for Samples from Reaction A (see Figs. 2 and 3)[a]

Sample	Time (h)	Conversion (mol%)
0	0	0
1	0.8	0.94
2	1.0	1.37
3	1.4	1.48
4	4.0	2.20
5	8.0	2.85
6	12.3	3.40
7	21.3	3.96
8	48.3	5.36
9	72.2	5.84
10	102.8	6.60
11	167.0	7.76

[a] The underlined samples are those most referred to in this work.

12 mm tubes and about 10-12 (w/v)% solutions in o-dichlorobenzene. The chemical shifts are relative to tetramethylsilane (Fig. 4). The calculations were carried out both by measuring the areas with a compensating polar planimeter and by weighing the areas cut out of photoreproductions of the spectra. The results obtained by both methods agree very well. Table 3 shows those obtained by the second method which seems somewhat more reproducible.

Polymer Degradation

Two methods were used to determine the degradation rate of the samples (Fig. 5). In the first, the HCl evolved both in the solid state and in solution in trichlorobenzene was estimated by conductivity measurements as described previously [8]. In the second, the loss of weight was followed by means of a very sensitive thermobalance (Perkin-Elmer TGS-2, equipped with a System 4 Microprocessor Controller). Both methods gave results in very good agreement. The values obtained for samples of Reaction A (Table 2) are those used in Figs. 6 and 7.

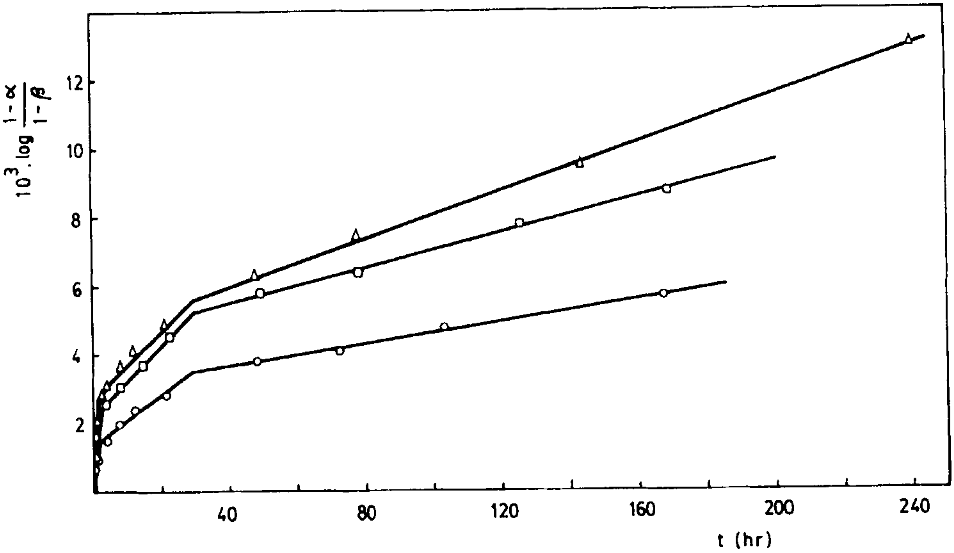

FIG. 3. Kinetic plots of nucleophilic substitution on PVC with sodium thiophenate: (○) Reaction A, (□) Reaction B, (△) Reaction C (see Table 1).

RESULTS AND DISCUSSION

The incorporation of thiophenate into the polymer is proved by UV spectroscopy, as shown in Fig. 1. Moreover, the change in the UV spectra with reaction time enables the kinetic features to be easily studied after a calibration curve has been determined.

The kinetic results of the substitution reaction at -15°C are shown in Figs. 2 and 3 and Table 1. It is clear from Fig. 2, which exhibits the conversion curves for reactant concentrations in Table 1, that the reaction is first order with respect to either the polymer or the nucleophile, even if some anomalies are observed in Reaction A as a result of the excess of nucleophile used (Table 1). (As some of the samples from Reaction A are those used for discussion in this section, the kinetic data are given in Table 2).

As illustrated by Fig. 3 (see Experimental Section), the reaction fits second-order kinetics, which suggests it to be an S_N2 substitution.

The plots in Fig. 3 make it clear that a three-step reaction is involved. Furthermore, the three steps are proved to be S_N2 processes as they all keep to second-order kinetics. Although a complete study of the kinetic features is now under way, we have calculated the three

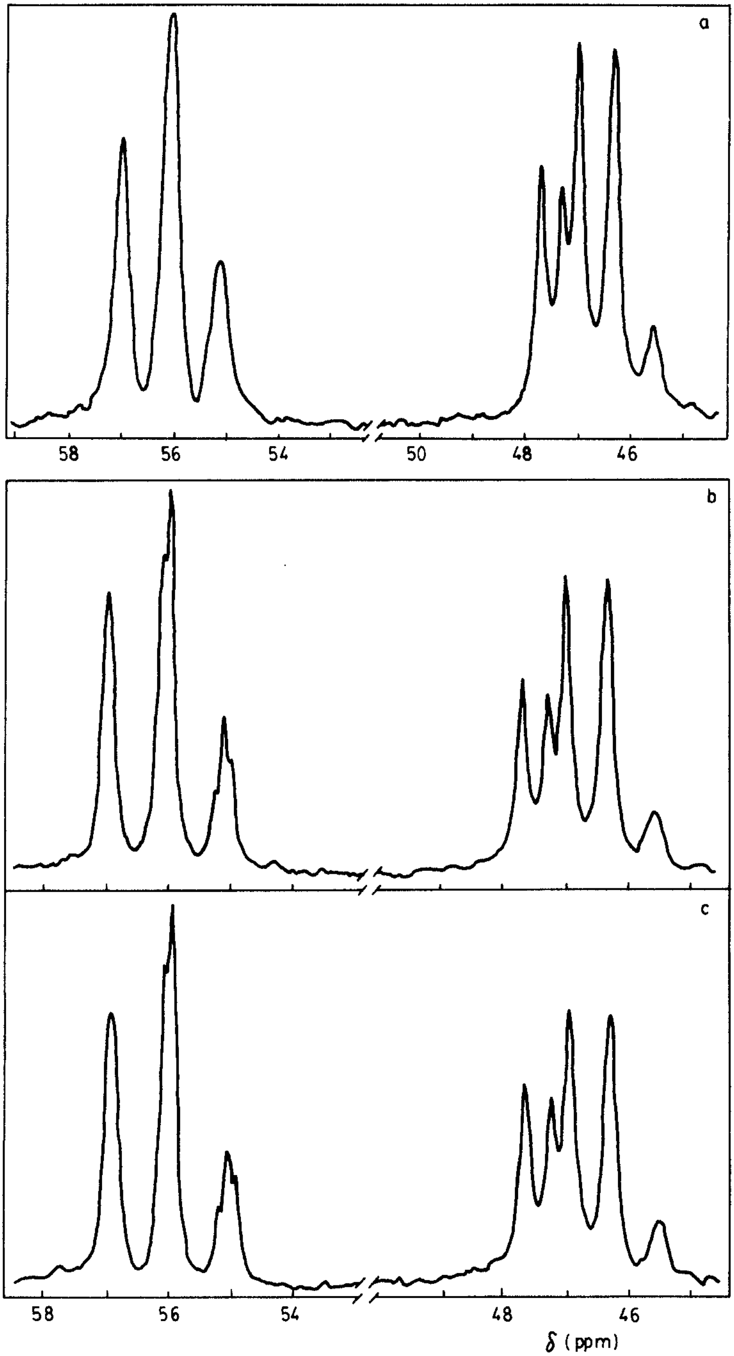

FIG. 4. ^{13}C-NMR spectra of Samples 0 (a), 2 (b), and 10 (c) (see Table 2).

TABLE 3. ^{13}C-NMR Tacticity Data[a]

Sample	Conversion (mol%)	P(SS)	P(SI&IS)	P(II)	P(S)	P(I)
0	0	.327	.475	.198	.565	.435
2	1.37	.347	.470	.183	.582	.418
10	6.60	.397	.454	.149	.624	.376

[a] P(SS): normalized values of syndiotactic triads.
P(II): normalized values of isotactic triads.
P(SI&IS): normalized values of heterotactic triads.
P(S): normalized values of syndiotactic dyads.
P(I): normalized values of isotactic dyads.
See Refs. 12-14.

reaction constants from the slopes of the straight lines. They are given in Table 1. Preliminary though these results are, one can see that the first reaction rate is about seventeenfold and sixtyfold that of the second and third steps, respectively.

The above results indicate the existence of a fraction of chlorine atoms which are much more reactive than the others in PVC. The former (about 2-3%) are those reacting by constant k_1; the latter are related to k_2 and k_3 processes.

The chlorine atoms in the "abnormal" structures considered in the literature [1] do not satisfy the best conditions for an S_N2 substitution, which are explained later in this section. This is particularly true for the allylic chlorine which is known to react through an S_N1 mechanism [11]. Consequently it seems reasonable to conclude that the reaction constant k_1 is related to some "normal" structures in PVC. As discussed later, the GTTG isotactic triad and the TTTG heterotactic triad exhibit the best conditions for S_N2 substitution.

The ^{13}C-NMR study of modified polymers obtained from Reaction A allows us to demonstrate that the higher the substitution extent, the lower is the isotactic and heterotactic triads content in the unreacted parts relative to that of syndiotactic triads. In order to simplify the discussion, we refer to the three samples 0, 2, and 10 of Reaction A; that is, the starting PVC and two samples whose modification extent lies on the end of the k_1 step and on the k_3 step, respectively (Table 2). As discussed later, they are also different in thermal degradation behavior.

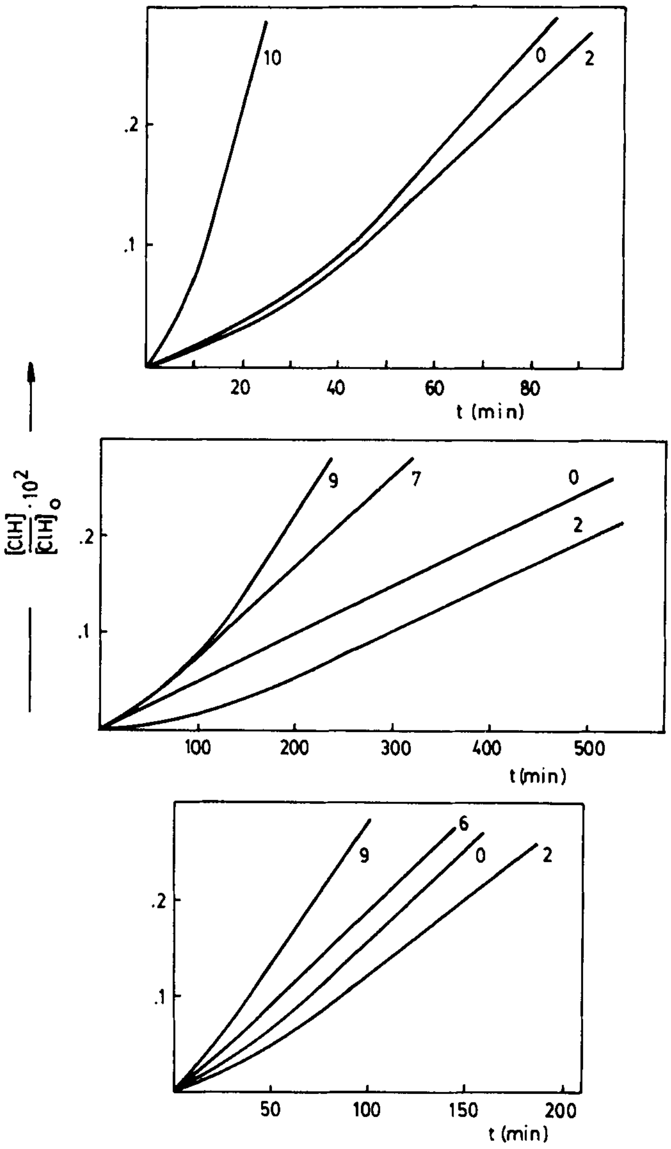

FIG. 5. Isotherms of degradation for the indicated samples from Table 2, degraded in solution at 180°C (upper), at 160°C (middle), and in the solid state at 180°C (bottom) ($[\mathrm{ClH}]/[\mathrm{ClH}]_o$ = molar fraction of HCl evolved).

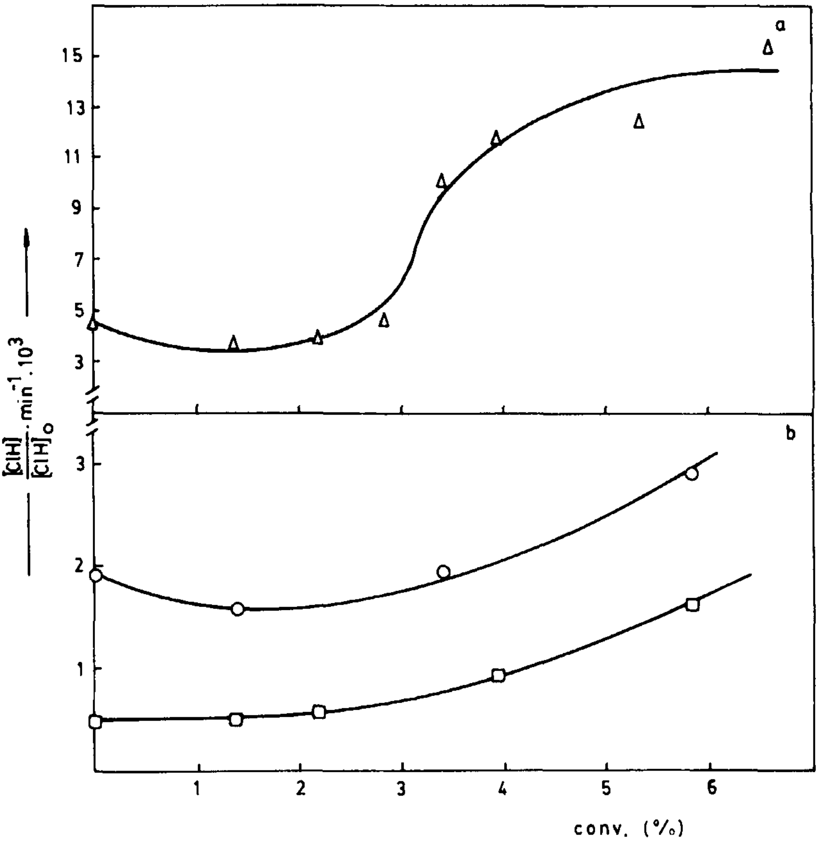

FIG. 6. Dependence of degradation rate of modified samples (Table 2) on degree of substitution: (△) degradation at 180°C in solid state, (○) degradation at 180°C in solution, (□) degradation at 160°C in solution. (Degradation values obtained by conductimetric measurements.)

From the planimeter measurements on ^{13}C-NMR spectra of the three samples chosen (Fig. 4), the normalized values of dyads and triads have been calculated by means of the conventional method [12, 13]. From the values obtained for dyads and triads (Table 3), it follows that the isotactic triads content and, to a lesser extent, that of heterotactic triads in the unreacted parts decrease with increasing substitution. Moreover, Samples 0 and 2 are similar in heterotactic content but the latter is significantly less isotactic than the former, which obviously suggests that at least some of the isotactic

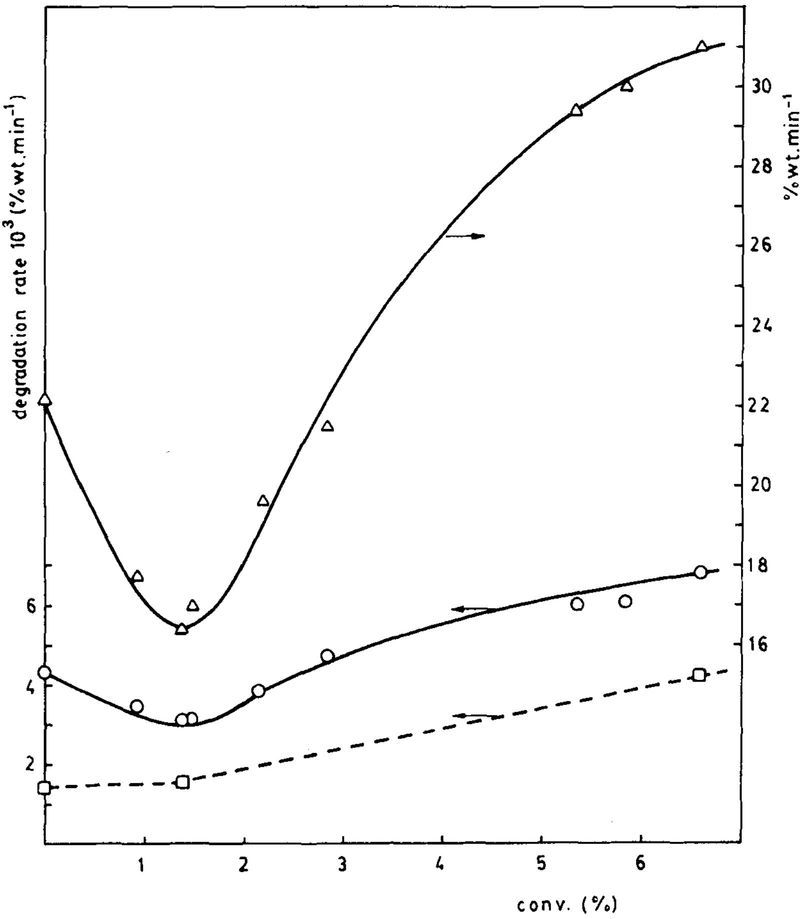

FIG. 7. Dependence of degradation rate of modified samples (Table 2) on degree of substitution: (△) 200°C, (○) 180°C, (□) 170°C. (Degradation values obtained in thermobalance.)

triads are more reactive from the very beginning of substitution (Step k_1). On the other hand, as indicated by values for Sample 10, some heterotactic triads react after the k_1 step is over while the isotactic ones keep on reacting. Consequently, some chlorine atoms in either the isotactic and/or heterotactic triads appear to be the most reactive in S_N2 substitution on PVC. Moreover, both types of chlorine atoms are not similar in reactivity since predominantly only the isotactic triads are the ones which react during the fast period, as illustrated by values in Table 3. In support of the above conclusions are the qualitative changes observed in the ^{13}C-NMR spectra of Fig. 4. In the light of these spectra it might be thought that during the k_1 step the band at about 55.1 ppm decreases more than that at 55.3 ppm (Spectrum b), contrary to what seems to occur for the subsequent steps (Spectrum c). If it were so, and taking into account that the above bands have been attributed to rmmr and mmmr pentads respectively [14], the greater reactivity of the GTTG isotactic triad (Fig. 11) would be proved. As a matter of fact, it is easy to show by means of atomic models that the rmmr pentad necessarily involves a GTTG triad. Nevertheless, the above ideas should be considered only as tentative suggestions until some further work, now under way, has been finished.

The influence of the thiophenate substitution on the thermal stability is shown in Figs. 5 to 7 where $[ClH]/[ClH]_0$ indicates the molar fraction of hydrogen chloride split-off. The slopes of the straight parts of the isotherms are taken as the degradation rates. As an example, Fig. 5 reproduces the conversion curves for a few samples from Reaction A degraded in solution at 160 and 180°C and in solid state at 180°C. The plots of the degradation rate as a function of the thiophenate substitution extent for the three sets of experiments are shown in Fig. 6. On the other hand, Fig. 7 represents the degradation rate for the same samples carried out in the thermobalance at 200, 180 and 170°C.

All the above results permit the following statements to be made: 1) the substitution results in slightly enhanced thermal stability provided that it does not surpass the k_1 step of the reaction; then the stability decreases with increasing substitution extent. 2) The expected decrease of degradation rates when the temperature is lowered appears to be surprisingly accentuated for Sample 0 so that, as shown in Figs. 6 and 7, it becomes somewhat more stable than Sample 2 at degradation temperatures of about 160-170°C.

The former conclusion obviously suggests that the first step of substitution involves the disappearance of labile structures which happen to be associated with certain isotactic placements. Conversely, the reason for the second conclusion is more difficult to understand if degradation rates are the only data to be taken into account. In principle, the enhanced increase in degradation rate with increasing degradation temperature for Sample 0 might be thought to be due to the occurrence of a cooperative initiation through the structures of higher activation energy than the labile ones; as a result, on decreasing the temperature the labile structures would degrade preferably and, of course, at a higher rate than Sample 2 which is supposed to contain less labile structures. But it is the opposite result that is really obtained. Hence the improved stabilization of Sample 0 at low temperatures in comparison with Samples 2 and 10 may only be explained by assuming that every labile structure gives rise to shorter polyenes than the more stable structures. The UV-VIS absorption spectra of degraded samples demonstrate this to be so, as described below.

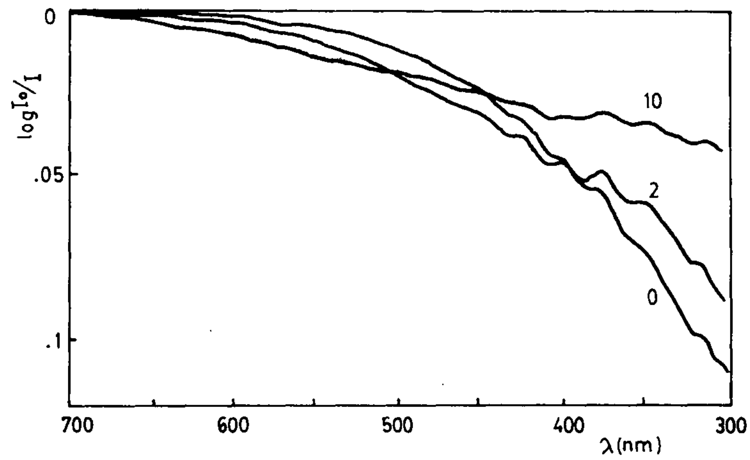

FIG. 8. UV-VIS absorption spectra of Samples 0, 2, and 10 (Table 2) degraded about 0.3% at 180°C in solid state.

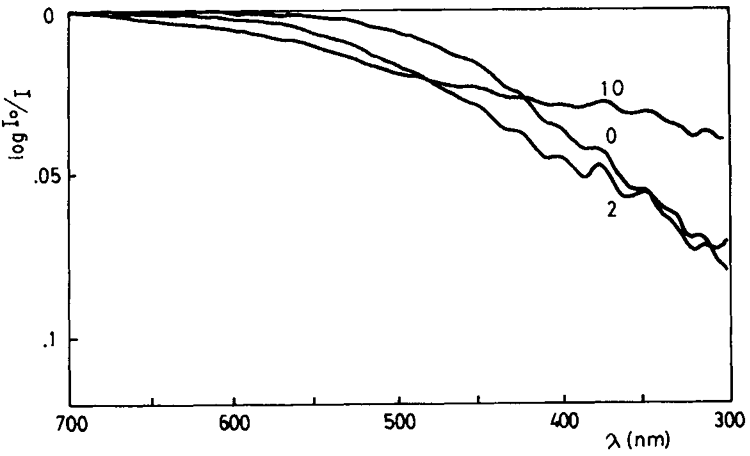

FIG. 9. UV-VIS absorption spectra of Samples 0, 2, and 10 (Table 2) degraded about 0.3% at 170°C in solid state.

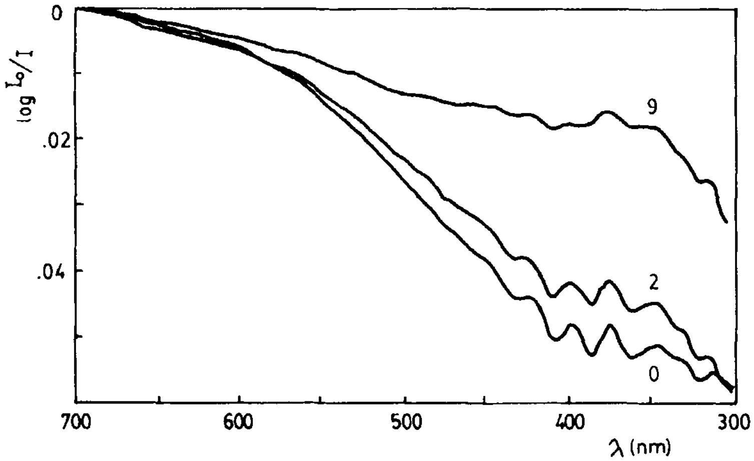

FIG. 10. UV-VIS absorption spectra of Samples 0, 2, and 9 (Table 2) degraded at 160°C in solution.

Figures 8, 9, and 10 show the UV-VIS spectra of the indicated samples degraded (0.3% molar) at 180 and 170°C in solid state and at 160°C in solution, respectively. The spectra in Figs. 8 and 9 make it evident, on the one hand, that the ratio

$$\frac{\text{absorbance at } \lambda < 400 \text{ nm}}{\text{absorbance at } \lambda > 400 \text{ nm}}$$

which is a measure of the ratio

$$\frac{\text{short polyenes } (n = 4\text{-}8)}{\text{long polyenes } (n = 8\text{-}12)}$$

markedly decreases with extent of substitution. On the other hand, the above ratio is independent of the degradation temperature for the modified polymers (curves for Samples 2 and 10 are superposable) but it clearly decreases with the temperature for the starting polymer (Sample 0). All these results confirm the above assumption that the degradation of the labile structures in Sample 0 results in a large build-up of the short polyenes relative to the long polyenes.

In contrast with what happens for Sample 0, it follows from the spectra of Sample 10 that the above quoted absorbance ratio is very

TABLE 4. Average Polyene Length for Samples Degraded in the Solid State [15]

	Average polyene length (number of double bonds)	
Sample	at 170°C	at 180°C
0	3.09	3.14
2	3.88	4.09
10	5.14	4.83

small, that is, the build-up of long polyenes is favored. This suggests that the high degradation rate of Sample 10 obeys an enhanced propagation process.

The above statements may be expressed by calculating the values of the average polyene length as described by Kelen et al. [15]. The values found are given in Table 4. Indeed, one can see that the average polyene length increases from the starting PVC to Sample 10 regardless of the degradation temperature.

The spectra of polymers degraded in solution (Fig. 10) are more difficult to interpret because Samples 0 and 2 show an enhanced absorption at all wavelengths of the spectrum. Nevertheless, the above indicated absorbance ratio, which is the only quantitative parameter valid for the analysis of the polyene spectra, decreases with increasing substitution, particularly during the k_2 and k_3 steps (Sample 9), thus indicating a behavior similar to that observed in the solid state. The enhanced absorption pointed out seems to be due to the contribution of the band at 450 nm which would overlap the fine spectrum of polyene distributions of either samples. The appearance of this band has already been reported by several authors [16-18] but no convincing explanation has ever been given. It has recently been found [19] that UV-VIS spectra of diluted solutions of the same degraded PVC change with time and that the shape of spectra, that is, the polyene distribution, depend on whether the solvent used is dichloromethane or tetrahydrofuran. In the former, the band at 450 nm is the most accentuated absorption while in the latter the polyene distribution is similar to that normally found in thermally degraded samples of PVC. Although the authors propose this to be related to the catalytic effect of ClH which would cause the formation of longer polyenes by the accumulation of short ones [19], it is worth noticing that since the solutions were obtained by extracting the soluble fractions with either solvents, it could very well be that the extracted fractions are really different in polyene distribution. Be that as it may, the fact that the abnormally high absorbance at 450 nm seems to accompany an accumulation of short polyenes supports our preliminary conclusions that

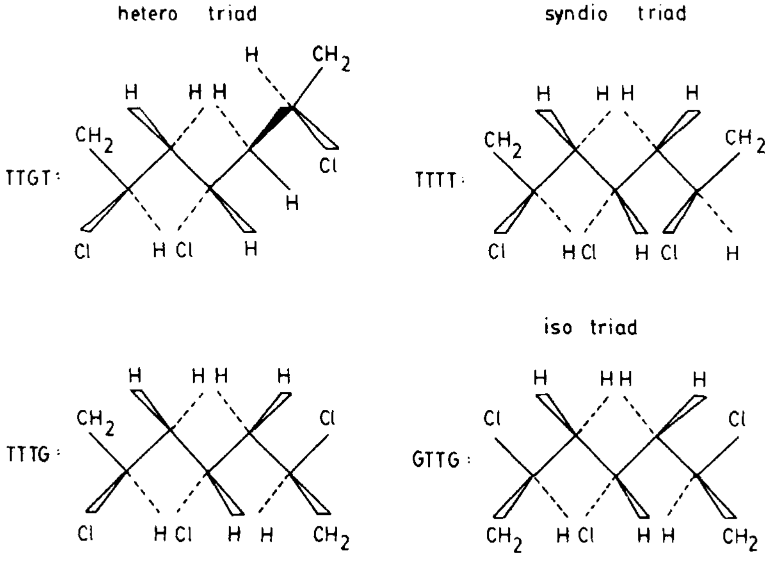

FIG. 11. Conformation of triads in PVC.

labile structures give rise to shorter polyenes relative to the more stable structures in PVC.

Taking into consideration the above results, the enhanced stability of Sample 2 may be attributed to the occurrence of an appropriate initiation-propagation equilibrium while Samples 0 and 10 behave as if this equilibrium was shifted toward either an easier initiation or a favored propagation, respectively.

It is worth noting that similar conclusions were drawn in one work of ours using polymer with a different tacticity [8].

The conclusions discussed so far may be further supported by taking into consideration the structure of the more frequent triads [10] among all the possible ones in PVC (Fig. 11). From observation of the isotactic triad GTTG, it follows that the chlorine atoms at carbons 2 and 6 have a much higher degree of freedom than that on atom 4. This makes it easy for the former Cl atoms to vibrate, thus giving rise to an easier initiation.

On the other hand, the central chlorine atom exhibits the best conditions for a backside S_N2 attack by a nucleophile: 1) there is no axial interaction of the nucleophile with groups larger than hydrogen atoms ; 2) the chlorine atoms on both neighboring units are as far as possible in PVC from the attack point; and 3) the transition state and, consequently, the central chlorine separation is favored by the fact that two H, Cl interactions are relieved.

Moreover, it is noted that the triad GTTG is forced to adopt the more stable conformation TTTT when S_N2 substitution occur. This results in the disappearance of the labile situation for the chlorine atoms at carbons 2 and 6.

Apart from heterotactic triad TTTG, none of the triads in Fig. 11 satisfies either the above conditions for S_N2 substitution or the labile situation of chlorine atoms. Even the TTTG isotactic triad is different from GTTG in that the former has only one chlorine in a labile situation and the chlorine atom on carbon 2 is much closer to the attack site than in the GTTG triad; consequently, the reactivity of the heterotactic triad TTTG must be lower than that of the GTTG isotactic triad. We must note that the above discussion is focused on the central carbon atom of each isolated triad. Needless to say, a similar discussion concerning the chlorine atoms on carbons 2 and 6 would be possible on condition that conformations neighboring upon either of the ends of the triads considered were known too.

The above considerations make it reasonable to correlate the reactivities of the triads GTTG iso and TTTG heterotactic with both the kinetic features in the substitution reaction and the changes in the thermal stability of modified polymers. As a matter of fact, the stabilization is easily understandable in terms of the elimination of labile conformations of the chlorine atoms while the increase in instability after a certain degree of modification might be due to the fact that the modified polymer becomes more and more abundant in TTTT sequences as a result of the substitution. The latter sequences have been claimed to favor the propagation process even if they are more resistant to the initiation [9].

Although much work has to be done in this field, the results of the present investigation show that the reasons for the instability of PVC lie, at least to a certain extent, in the normal structure of the polymer.

REFERENCES

[1] Z. Mayer, J. Macromol.-Sci. Rev. Macromol. Chem., C10, 263 (1974).

[2] G. Ayrey, B. C. Head, and R. C. Poller, J. Polym. Sci., D, 8, 1 (1974).

[3] D. Braun, Degradation and Stabilisation of Polymers, Applied Science Publishers, London, 1975, p. 23.

[4] W. H. Starnes, Jr., Adv. Chem. Ser., 169, 309 (1978).

[5] J. Millán, E. L. Madruga, M. Bert, and A. Guyot, J. Polym. Sci.-Polym. Chem. Ed., 11, 3299 (1973).

[6] J. Millán, E. L. Madruga, and G. Martinez, Angew. Makromol. Chem., 45, 177 (1975).

[7] G. Martinez, J. Millán, M. Bert, A. Michel, and G. Guyot, J. Macromol. Sci. Chem., A12, 489 (1978).

[8] G. Martinez, C. Mijangos, J. Millán, D. L. Gerrad, and W. F. Maddams, Makromol. Chem., 180, 2937 (1979).

[9] J. Millán, G. Martinez, and C. Mijangos, J. Polym. Sci., Polym. Chem. Ed., 18, 505 (1980).

[10] D. Doskocilová, J. Štokr, B. Schneider, H. Pivcová, M. Kolinsky, J. Petránek, and D. Lim, J. Polym. Sci., C, 16, 215 (1967).

[11] A. Burille, Doctorate Thesis, University of Lyon, France, 1979.

[12] Q. Pham, J. Millán, and E. L. Madruga, Makromol. Chem., 175, 945 (1974).

[13] A. H. Abdel-Alim, J. Appl. Polym. Sci., 19, 1227 (1975).

[14] C. J. Carman, Macromolecules, 6, 725 (1973).

[15] T. Kelen, G. Bálint, G. Galambos, and F. Tüdős, Eur. Polym. J., 5, 597 (1969).

[16] D. Braun, Pure Appl. Chem., 26, 173 (1971).

[17] G. Palma and M. Carenza, J. Appl. Polym. Sci., 16, 2485 (1972).

[18] J. Verdu, Private Communication, 1980.

[19] E. D. Owen, I. Pasha and F. Moayyedi, J. Appl. Polym. Sci., 25, 2331 (1980).