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COMPUTER SIMULATIONS OF MICROSTRUCTURE CHANGES RESULTING FROM THE THERMAL DEGRADATION OF PVC

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ABSTRACT

Recent studies of the dehydrochlorination of PVC in the solid state offer convincing evidence in support of a mechanism that involves initiation at *gttg*$^-$ conformations in isotactic stereosequences generally considered to be normal units. Attempts have been made to verify such a mechanism by direct measurements, using solution ^{13}C NMR, of the changes in tacticity that result from the degradation. In this paper, computer simulations are reported that use Monte Carlo methods to simulate preferential degradation at isotactic sequences of various minimum sequence lengths. The results indicate that at the levels of degradation accessible to experimental verification by solution NMR ($<2\%$), the predicted changes in triad probabilities are close to the limits of experimental error and are not a sensitive indicator of the mechanism. The simulations also indicate that for the degradation to result in polyene sequence lengths that correspond to experimentally determined values requires that the dehydrochlorination include some atactic and syndiotactic sequences which, in turn, reduces the changes in P_{mm}. On the other hand, there are some indications that more specific indications can be

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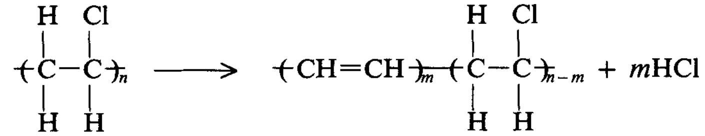
obtained from the changes in the probabilities for pentads and longer sequences, provided that appropriate NMR data can be generated.

INTRODUCTION

Upon exposure to temperatures as low as 100 to 120°C [1, 2], poly(vinyl chloride) undergoes dehydrochlorination to form polyene sequences consisting of as many as 20 conjugated double bonds. The reaction can be represented by



$$\left(\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{Cl}}{\underset{\text{H}}{\text{C}}}\right)_n \longrightarrow \left(\text{CH}=\text{CH}\right)_m\left(\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{Cl}}{\underset{\text{H}}{\text{C}}}\right)_{n-m} + m\text{HCl}$$

Even relatively small amounts of the long polyene sequences can cause discoloration and a breakdown of physical properties, i.e., a loss of mechanical, electrical, and optical properties. The thermal instability is somewhat surprising in view of the fact that low-molecular-weight model compounds for PVC, e.g., 2,4-dichloropentane or 2,4,6-trichloroheptane, are relatively stable organic compounds with HCl elimination becoming significant only at temperatures >300°C [1-5]. Over the years many studies have been made with the express goal of developing an understanding of the mechanism of the dehydrochlorination in PVC. It is now generally accepted that, following the initial reaction, the polyenes result from a "zipper" mechanism, i.e., the first double bond activates the formation of an adjacent conjugated double bond, and so on, until extended polyene sequences are formed. The two preferred mechanisms that have been proposed to account for this "zipper" reaction are the ion-pair mechanism [5-7] and the free-radical mechanism [8, 9].

Of the many ideas that have been proposed to rationalize the instability of PVC, currently two competing theories tend to dominate: 1) Abnormal or irregular structures are the major cause; and 2) Local conformations that are related to isotacticity tend to favor HCl elimination. Numerous studies have sought to determine the effects on thermal stability that result from the presence of irregular structures in PVC, e.g., head-to-head structures, branches (chloromethyl, 2-chloroethyl, and butyl groups) or, more specifically, branches that result in tertiary chlorines, internal and chain end unsaturation (allylic chloride), and groups containing oxygen [6, 10-12]. Because these defect structures are low in content, it is difficult to identify their relative roles. Furthermore, the effects of changes in their concentrations, generally achieved by varying the polymerization conditions, are not easily correlated with the changes in the thermal stability of PVC because of other concomitant structural changes. It is not surprising then that there is considerable controversy concerning the nature, concentration, and relative importance of these irregular structures. For example, evidence presented by Hjertberg and Sörvik [13-15] indicates that the most frequently occurring tertiary chlorine is also the most important labile structure. On the other hand, Minsker et al. [16] claimed that internal unsaturation is of primary importance.

Recently, a strong case was developed by Millán and coworkers that the thermal degradation involves initiation at *ggtg*$^-$ conformations of isotactic stereosequences, previously considered to be normal units [15, 17-31]. In part this is based on the observation that the rate of degradation of solid PVC depends on the tacticity, at least within range $0.36 < P_m < 0.46$ that is accessible to usual polymerization methods [21-23, 26, 29, 32]. Furthermore, studies [33] of the kinetics of the dehydrochlorination between 110 and 190°C yielded Arrhenius plots with two well-differentiated slopes, corresponding to activation energies of 29 (at low temperatures) and 84 $kJ \cdot mol^{-1}$. It was suggested that this behavior reflects two different processes, initiation at the labile *gttg*$^-$ isotactic triad conformation or random degradation at any stable chlorine atom along the chain.

A more direct approach to determining the role of isotactic triads as initiating sites were studies of PVC modified by nucleophilic substitution with sodium benzenethiolate [24, 25, 34-36] which occurs preferentially at isotactic triads in the *gttg*$^-$ conformation, with exclusive attack at the central chlorine atom. It was shown that the degradation rate decreases strongly as the degree of substitution increases up to about 0.8% conversion [27], which corresponds closely with the content of *gttg*$^-$ conformations in the original polymer. Further modification had minimal effect on the thermal stability. The polyene distribution was also found to be strongly affected by the degree of substitution. In a recent detailed study by Millán and coworkers which included analyses of appropriate IR absorption peaks, results were presented that led them to conclude that "This behavior provides conclusive support for our proposal that the initiation of the thermal degradation in PVC is due, to the greatest extent, to the occurrence of the *gttg*$^-$ conformation either during the polymerization or during the degradation process as a result of thermally induced conformational changes" [37].

In light of our interest in PVC microstructure [38, 39], we considered the possibility that NMR analysis could be used to obtain direct measurements of changes in PVC tacticity that might be expected from preferred initiation in isotactic sequences. Indeed, Millán et al. [32] have already reported some "tentative" measurements of tacticity changes derived from highly resolved ^{13}C-NMR spectra of thermally degraded PVC samples. Their results indicated that during the initial stages of degradation the contents of the syndiotactic and heterotactic triads remain unchanged while the decrease in isotactic triad content is appreciable, although the observed changes were acknowledged to lie very close to the limits of experimental uncertainties. They concluded that "the very labile structures in PVC are some chlorine atoms located mainly at the normal but little frequent *gttg*$^-$ isotactic triad conformation," specifically those of the *mmmr* and *rmmr* pentads.

In this paper we report tacticity changes derived from computer simulations, based on Monte Carlo methods, of the preferential dehydrochlorination of isotactic stereosequences. In these considerations, possible initiating sites were restricted to labile chlorines located at various isotactic configurations. The goal of these studies was to determine the magnitude of the changes in tacticity that can be expected from a theoretical point of view. The results are compared to the so-called "tentative" tacticity changes reported previously by Millán and coworkers [32] for the thermal degradation of PVC in the solid state.

COMPUTER SIMULATIONS

The simulations were made using a Pascal program described in detail in Appendix A. It is an extension of the program described elsewhere [40]. It uses Monte Carlo methods to simulate first the polymerization of vinyl chloride to produce a PVC of specified P_m and then its random dehydrochlorination, according to specified parameters. Specifically, it performed the following main tasks:

1. It generated Bernoullian chains according to entered values of P_m, the degree of polymerization, DP, and the number of molecules, N.
2. It determined the dyad, triad, tetrad, and pentad probabilities.
3. It counted the number of isotactic and syndiotactic sequences containing exactly n_i and n_s repeat units, respectively.
4. According to entered values of a minimum isotactic length, n_i, and percent degradation, it randomly located and degraded isotactic sequences that contain n_i or higher repeat units.
5. It calculated average values of the dyad, triad, tetrad, and pentad probabilities after the degradation.
6. It counted the number of double bonds of various sequence lengths ($n_=$ repeat units) and calculated the average double bond length that resulted from degradation.

As reported previously [40], the program was tested stringently for effects of sample size and conformation to Bernoullian statistics. Analysis of the results showed that sample size and chain-end effects can be conveniently eliminated by keeping the product of DP and number of molecules (DP × N) to a value of 1,000,000. Although this value appears to be high, the dependency P_m needs to be considered, i.e., the larger the P_m value deviates from randomness ($P_m = 0.5$), the larger the product must be. For example, for a P_m value of 0.5 the product DP × N must be greater than 50,000, whereas for $P_m = 0.9$ the product must be greater than 400,000.

RESULTS AND DISCUSSION

Degradation of Isotactic Sequences

The initial chains were simulated in such a manner as to mimic the properties of a typical commercial PVC sample (e.g., Esso 366 industrial resin) with DP = 600 and $P_m = 0.45$. By design the initial computer simulations involved selective degradation of *isotactic* units. This represents the extreme case in which the process ignores the role of sequence conformation. While it is well known that not all isotactic sequences populate the *gttg*$^-$ conformation [37], this model does not concern the fraction of isotactic sites since this would only affect the rate, not the magnitude of observed changes in tacticity. Ignoring the role of conformation and the impact of other concomitant random elimination of HCl results in the maximum observable changes in the isotactic units.

In the first set of simulations, degradation of the isotactic sequences was unconstrained by the sequence length. The program randomly selected a site at which elimination occurred *only* when it appeared in an isotactic (*m*) environment, irrespective of length. The elimination proceeded in both directions from the random site and was terminated when it encountered a syndiotactic dyad (*r*). Typical results are shown in Fig. 1, which is a plot of the difference in probabilities for the triad stereosequences, *P*(degraded)-*P*(nondegraded), as a function of the percent degradation. The most striking feature is that in spite of the selective elimination of isotactic sequences, the relative changes in the probabilities of the *mm* triad se-

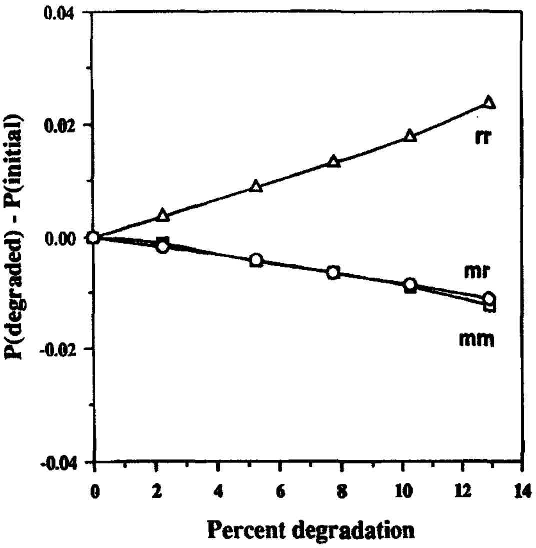
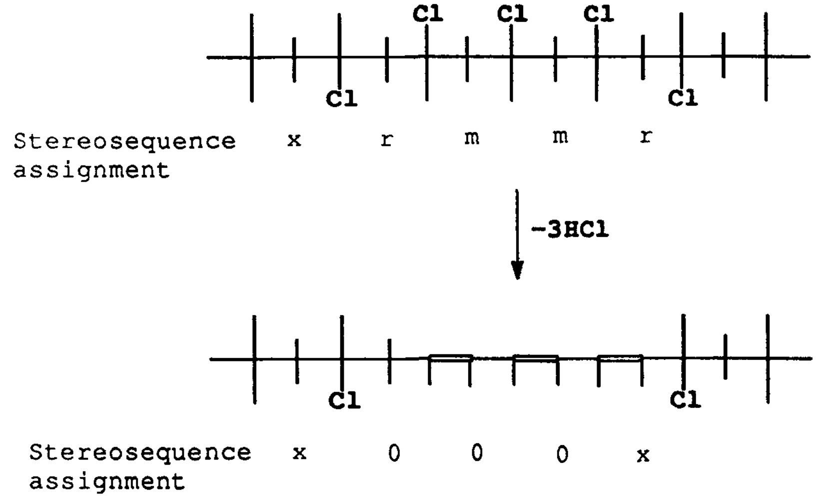


FIG. 1. Changes in triad probabilities, isotactic *mm* (□), atactic *mr* (○), and syndiotactic *rr* (△), before and after degradation of isotactic dyads and above.

quences are small. For example, even at 10% degradation the changes in the *mm* probabilities are ca. 0.01. Furthermore, the probabilities of both isotactic (*mm*) and atactic (*mr*) triads decrease while the syndiotactic triads (*rr*) actually increase.

This behavior can be rationalized by considering the two effects that accompany the selective elimination of isotactic units: 1) The total number of dyads and triads decreases, so the probability or relative frequency of the units that are not degraded, e.g., *rr*, will increase; and 2) Sequence end effects associated with the degradation of isotactic units are important. According to the constraints chosen for the simulation, each isotactic sequence is terminated by a syndiotactic dyad at either end. However, as a result of the elimination of the isotactic units, these syndiotactic dyads also lose their designation. For example, as shown in Scheme 1, the degradation of an isotactic triad results in the elimination of two meso and two racemic dyads. As a result of the decrease in the total number of dyads, the values of P_m and P_r remain unchanged. For the triads a total of five stereosequences are lost, i.e., *xr*, *rm*, *mm*, *mr*, and *rx*, where *x* can be either *m* or *r*. For simplicity, if P_m = 0.5 the two *xr* triads will on average correspond to one syndiotactic (*rr*) and one atactic (*rm*) triad. Therefore, selective degradation of isotactic triads involves the removal of 1 *mm*, 3 *mr*, and 1 *rr* sequences, i.e., it results in an increase in P_{mm} and P_{rr} and a decrease in P_{mr}. The results of similar considerations for the selective elimination of longer isotactic units are summarized in Table 1. Apparently there is a turning point in trends for the degradation of isotactic tetrads. For selective elimination of isotactic sequences of this length and greater, both P_m and P_{mm} decrease and P_r and P_{rr} increase, while P_{mr} begins to increase only for the selective degradation of isotactic pentads and above.

The results of the computer simulation presented above obviously refer to a somewhat more complicated situation. The P_m value was not 0.5 nor was the simu-



SCHEME 1.

lated degradation restricted to isotactic units of a specific length. Comparison of the computed changes with the predictions given in Table 1 suggests that the simulation approximates a degradation of isotactic units between triads and tetrads, on the average. Indeed, the resulting average double bond length was determined to be 3.3.

Further simulations were made to determine the effect of increasing the minimum length of the isotactic sequence to be degraded. The changes in the triad stereosequence probabilities for simulations that are constrained to the random degradation of isotactic units longer than or equal to triads, tetrads, and pentads are shown in Fig. 2. For the pentads the extent of degradation does not exceed 4% because statistically not all chains have isotactic units of sufficient length. In general, the values of P_{mm} decrease in all of these simulations while the values of P_{rr} increase. However, the value of P_{mr}, which decreased for random elimination of

TABLE 1. Predicted Changes[a] in Dyad and Triad Probabilities as a Consequence of Degrading Isotactic Units of an Exact Length

Units degraded	P_m	P_r	P_{mm}	P_{mr}	P_{rr}
rmr	+	−	+	−	=
rmmr	=	=	+	−	+
rmmmr	−	+	−	=	+
rmmmmr	−	+	−	+	+
rmmmmmr	−	+	−	+	+
rmmmmmmr	−	+	−	+	+

[a] The changes in probability are denoted by +, −, or = which indicate an increase, decrease, or identical probabilities, respectively.

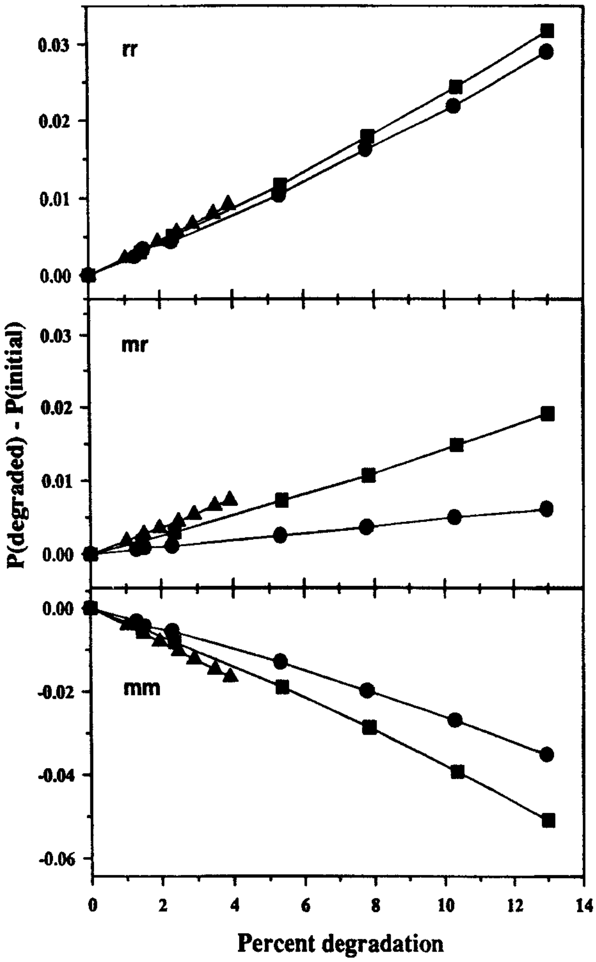


FIG. 2. The effects of changes in minimum isotactic sequence length on the changes in triad probabilities: triads and longer (●), tetrads and longer (■), pentads and longer (▲).

dyads and above (Fig. 1), commences to increase for degradations involving isotactic triads and above. In all cases the changes are quite small, e.g., a 2% degradation of isotactic pentads and above results in a change in the *mm* triad that is <0.008 (the value decreases as the minimum isotactic length decreases). Since substantial crosslinking occurs at 2% degradation in the solid state, the higher extents of dehydrochlorination are generally not accessible to experimental verification by solution NMR.

Similar plots were constructed, Fig. 3, for the concomitant changes in the probabilities for the pentad stereosequences with isotactic centered triads, i.e., *mmmm*, *mmmr*, and *rmmr* pentads. These plots reveal that in each of the simulations, regardless of minimum sequence length, the probability for *mmmm* sequences diminishes with increased extent of degradation. However, a greater decrease is observed as the minimum sequence length for degradation increases. A similar

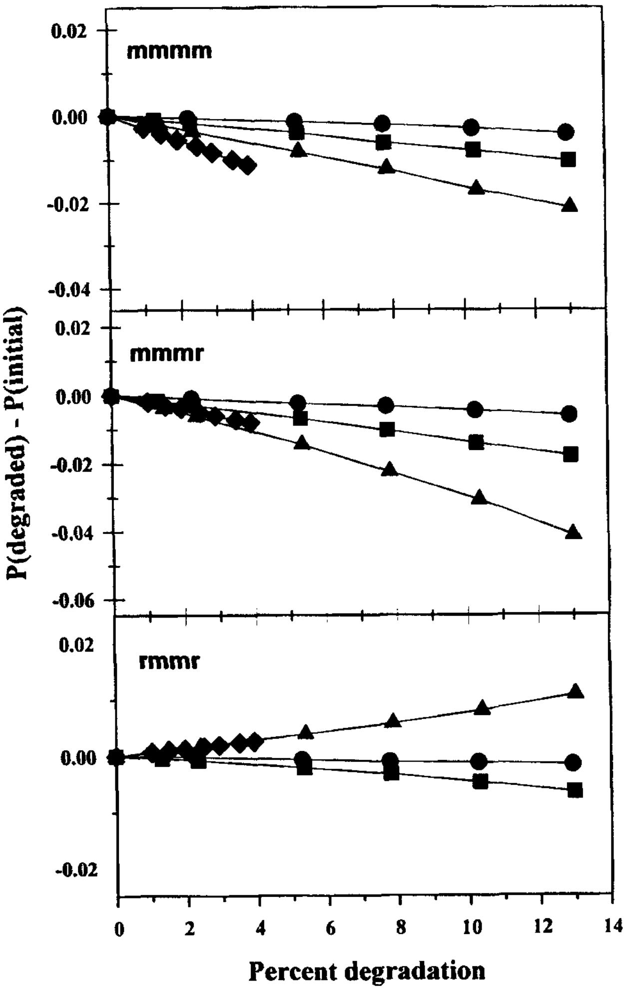


FIG. 3. The effects of changes in minimum isotactic sequence length on the changes in various pentad probabilities: dyads and longer (●), triads and longer (■), tetrads and longer (▲), pentads and longer (◆).

pattern is seen for the *mmmr* sequences up to a minimum specification of tetrads; the reduction in P_{mmmr} is less when the minimum sequence length is a pentad than when it is a tetrad. For degradation involving isotactic dyads and triads, the value of P_{rmmr} decreases. However, when the length of the minimum is tetrads and above, the probability of *rmmr* pentads shows a sharp increase as a result of degradation and then remains relatively unchanged for pentads and longer. This is as expected, since they are of shorter length than the specified minimum.

Comparison with Experimental Results

As described in the Introduction, Millán et al. [32] reported "tentative" measurements of the tacticity changes that result from the thermal degradation of PVC in the solid state. Samples taken prior to and after degradation to a 0.8% level, at 180°C, were dissolved in dioxane so that highly resolved ^{13}C-NMR spectra were obtained. This allowed them to accurately determine peak areas, by integration, and to compute not only the *mm*, *mr*, and *rr* triad probabilities but also those for the *mmmm*, *mmmr*, and *rmmr* pentads. Based on the results compiled in Table 2, they concluded that "syndiotactic or heterotactic triads change. In contrast, the decrease in isotactic triad appears to be appreciable, even if the observed changes lie at the limit of the experimental uncertainties." For the isotactic pentads, the *mmmr* and *rmmr* pentads appeared to decrease while the *mmmm* pentads remained unchanged. Based on these results, and indications from previous work that the chlorines located at —*mmr*— sequences with a $gttg^-$ conformation are labile, they concluded that the labile chlorines are those of the *mmmr* and *rmmr* pentads.

To facilitate a direct comparison with the results reported by Millán et al. [32], computer simulations were performed with a similar extent of degradation (0.85 to 1.01%). As before, the simulations specified *minimum* isotactic sequences lengths, i.e., dehydrochlorination could occur only when the randomly selected site comprised an isotactic sequence of length equal to or longer than the specified value. Again, conformational effects were ignored. The results for these simulations are summarized in column 2 of Table 3. The key features are: 1) The changes in the triad probabilities are small and reach magnitudes that are measurable by NMR only for selective degradation of isotactic sequences that are at least tetrads and longer. 2) The decrease in the *mm* triad probability (0.007) reported by Millán et al. is considerably larger than any corresponding changes obtained in the simulations. The largest decrease in the *mm* triad is 0.0042, which was obtained for the specific degradation of isotactic pentads and above. However, for this simulation the atactic and syndiotactic triads increase, in contrast to the experimental results. 3) A decrease in all three pentad probabilities, reported for the experimental results, occurs only when the simulations include isotactic units of a smaller length (dyads or triads and above). For the simulations of the degradation that specified longer minimum isotactic units (tetrad or pentads and above), the probability for *rmmr* sequences begins to increase. Furthermore, in no simulation did the *mmmm* pentad content remain constant while the *mmmr* and *rmmr* contents decrease, as reported by Millán et al.

At least two explanations can be presented to account for this discrepancy: 1) Because of the magnitude of the experimental uncertainties, incorrect trends were

TABLE 2. Tacticity Changes in Triad and Isotactic Pentad Probabilities as a Consequence of Thermal Degradation of PVC Up to 0.8% at 180°C as Reported by Millán et al. [32]

	mm	*mr*	*rr*	*mmmm*	*mmmr*	*rmmr*
Initial	0.204	0.493	0.303	0.043	0.098	0.063
Degraded	0.197	0.492	0.302	0.043	0.094	0.060
Change	−0.007	−0.001	−0.001	0	−0.004	−0.003
Degraded[a]	0.199	0.496	0.305	0.043	0.095	0.061
Change[a]	−0.005	0.003	0.003	0	−0.003	−0.002

[a] After normalization.

TABLE 3. Computer Simulated Tacticity Changes in Triad and Isotactic Pentad Probabilities as a Result of Degrading Isotactic Units Above a Minimum Length

Stereosequence	Difference[a]	Difference[b]	Difference[c]
	Isotactic Triads and Above		
P_{mr}	+0.0004	+0.0002	+0.0003
P_{mm}	−0.0022	−0.0015	−0.0016
P_{rr}	+0.0019	+0.0013	+0.0013
P_{mmmm}	−0.0007	−0.0003	−0.0005
P_{mmmr}	−0.0012	−0.0009	−0.0008
P_{rmmr}	−0.0004	−0.0003	−0.0003
	Isotactic Tetrads and Above		
P_{mr}	+0.0011	+0.0008	+0.0010
P_{mm}	−0.0028	−0.0026	−0.0028
P_{rr}	+0.0018	+0.0018	+0.0018
P_{mmmm}	−0.0013	−0.0012	−0.0012
P_{mmmr}	−0.0021	−0.0021	−0.0022
P_{rmmr}	+0.0006	+0.0005	+0.0006
	Isotactic Pentads and Above		
P_{mr}	+0.0019	+0.0018	+0.0018
P_{mm}	−0.0042	−0.0035	−0.0040
P_{rr}	+0.0023	+0.0016	+0.0022
P_{mmmm}	−0.0028	−0.0025	−0.0027
P_{mmmr}	−0.0020	−0.0020	−0.0020
P_{rmmr}	+0.0007	+0.0005	+0.0007

[a] Random selection of isotactic units, degree of degradation = 0.95%.

[b] Degradation of 8 units beginning with an *mmr* sequence, degree of degradation = 1.34%.

[c] Degradation of 8 units beginning at the center of an isotactic sequence, degree of degradation = 1.33%.

concluded by Millán et al.; or 2) The simulation does not adequately represent the actual degradation process. These are considered in more detail below.

In regard to the reliability of the data, it is of note that for the degraded sample the sum of the triad probabilities is 0.991, rather than 1.000 as required. To a first approximation this can be dealt with by normalizing the data. The resulting changes in triad probabilities, shown in Table 2, are in fairly good agreement with the simulations, particularly as the minimum length of isotactic sequence is increased. However, in no simulation did the *mmmm* pentad content remain constant, which is inherent to the model. Similarly, the experimentally observed decrease in *rmmr* pentad content is observed in the simulations only when the degradation includes the isotactic triads, in apparent conflict with the changes in triad probabilities. Perhaps the most striking result is the relatively good agreement that is obtained for the *mmmr* pentads. Perhaps it is of note that the isotactic *mmmr* pentads are also directly linked with the *gttg*$^-$ isotactic triads specified by Millán et al. [32].

Changes in Sequence Length

Concerning the validity of the parameters used for the simulation, it is of note that the Millán group has shown, by UV-visible analyses, that the average polyene sequence length is between 7 and 9 bonds [32]. By comparison, the average polyene sequence lengths obtained in the simulation for the preferential degradation of dyads, triads, tetrads, and pentads and above were 3.3, 4.2, 5.1, and 6.1, respectively. Although these values do not match the experimental results, clearly the mechanism chosen for the simulations will result in the maximum possible changes in *mm* triad content. Any mechanism that includes syndiotactic configurations as part of the sequence necessarily results in smaller changes in P_{mm}.

To explore this matter further, computer simulations were made of two other degradation mechanisms: 1) Random selection of isotactic units equal to or longer than a specified minimum length followed by dehydrochlorination of eight units beginning at the *mmr* sequence (column 3, Table 3); 2) Random selection of isotactic units equal to or longer than a specified minimum length followed by dehydrochlorination, beginning at the center of the sequence and removing four HCl units equally in both directions (column 4, Table 3). These simulations should better approximate the mechanism proposed by Millán et al. in that degradation is initiated at an —*mmr*— sequence. Furthermore, it is also more realistic since it takes into account the observed average double bond length [41]. A somewhat higher extent of degradation (1.33%) was obtained in these simulations. Yet, as suggested above, the changes in the various probabilities are smaller than or equal to those obtained in the simulation involving the degradation of isotactic units only (column 2, Table 3). Perhaps more importantly, the observed trends for the changes are unaffected.

CONCLUSIONS

This paper presents computer simulations that test the feasibility of direct verification by NMR of the hypothesis that the macromolecular microstructure is of importance in the initiating step of the thermal degradation mechanism of PVC. These simulations determined the changes in sequence probabilities that result from the selective dehydrochlorination of randomly selected isotactic units with a specified minimum length in PVC chains of DP = 600 and P_m = 0.45. The overriding conclusion is that, regardless of the choice of the minimum length for the isotactic sequences to be degraded, the resulting changes in the probabilities are small at the levels of degradation ($\leq$2%) that are accessible to experimental verification by solution NMR measurements. At higher levels of degradation of PVC the concomitant crosslinking reaction renders the samples insoluble. In particular, it appears that the changes in *triad* probabilities as determined by NMR methods probably will not permit an unambiguous assessment of the role of tacticity in the thermal degradation of PVC. Indeed, further improvements in the quality of the NMR data, either by devising a means of extending the accessible range of dehydrochlorination or by obtaining improved spectral resolution, are unlikely to solve this dilemma since there are inherent limitations to the changes in the values P_{mm}, P_{rr}, and P_{mr}. These limitations are intrinsically linked to the statistical distributions of configurational sequences in a Bernoullian polymer. On the other hand, there are some indications that the direct measurements of probabilities for pentads or longer sequences may offer better insight. Unfortunately, these are also subject to greater experimental uncertainty due to smaller absolute values and the difficulties in resolution of the various peaks.

Nevertheless, it is important to realize that the arguments presented above refer to the experimental verification of tacticity changes that can be expected for selective dehydrochlorination of isotactic stereosequences. This should not be construed as evidence that a mechanism which includes preferential initiation at sites of a specific configuration is incorrect. Indeed, the various forms of evidence offered by the Millán group still present compelling evidence in support of such a mechanism which must be assessed on its own merit.

APPENDIX A

The logic of this program is best understood by following the program structure as illustrated by the flowchart shown in Fig. 4. It commences by allowing the user to enter the desired value of P_m, the degree of polymerization, DP, and the number of molecules, N, to be generated, the percent degradation, %deg, and the minimum isotactic length to be degraded, ni. Random numbers ranging from 0 to 1 are then generated and, according to the entered P_m value, are rounded off to integral values of 0 or 1 and stored in a one-dimensional array called **configuration**. This mimics a polymerization reaction where a 0 denotes a unit in the chain with one configuration and a 1 denotes a unit of the opposite configuration. The random number generator continues until the designated degree of polymerization has been attained. Once the chain has been polymerized to the desired degree of polymerization, the contents of the array **configuration** are examined and, accordingly, the character *m* or *r* is stored in a new one-dimensional array called **configuration_m_r**. Whether a unit will be designated as an *m* or *r* sequence is better understood by considering the chain in terms of doublets. Since two adjacent units of a doublet are said to form a meso configuration if both units have the same handedness, units of two adjacent zeros (00) or ones (11) are designated as an *m* configuration (isotactic sequence). Similarly, units of opposite handedness, (01) or (10), are designated as an *r* configuration (syndiotactic sequence). It should be noted that the elements of the array **configuration_m_r** will be one less than that of the array **configuration**.

The program then randomly searches the array **configuration** until it locates an isotactic sequence equal to or greater than the minimum limit set by the user. These units are degraded by replacing the numerical values by the number 2. Degradation continues until the desired percent degradation, also entered by the user, has been attained. The contents of the array **configuration** are examined and, accordingly, the character *m*, *r*, or = is stored in the one-dimensional array called **configuration_m_r**. The contents of this array are examined and the number dyads and

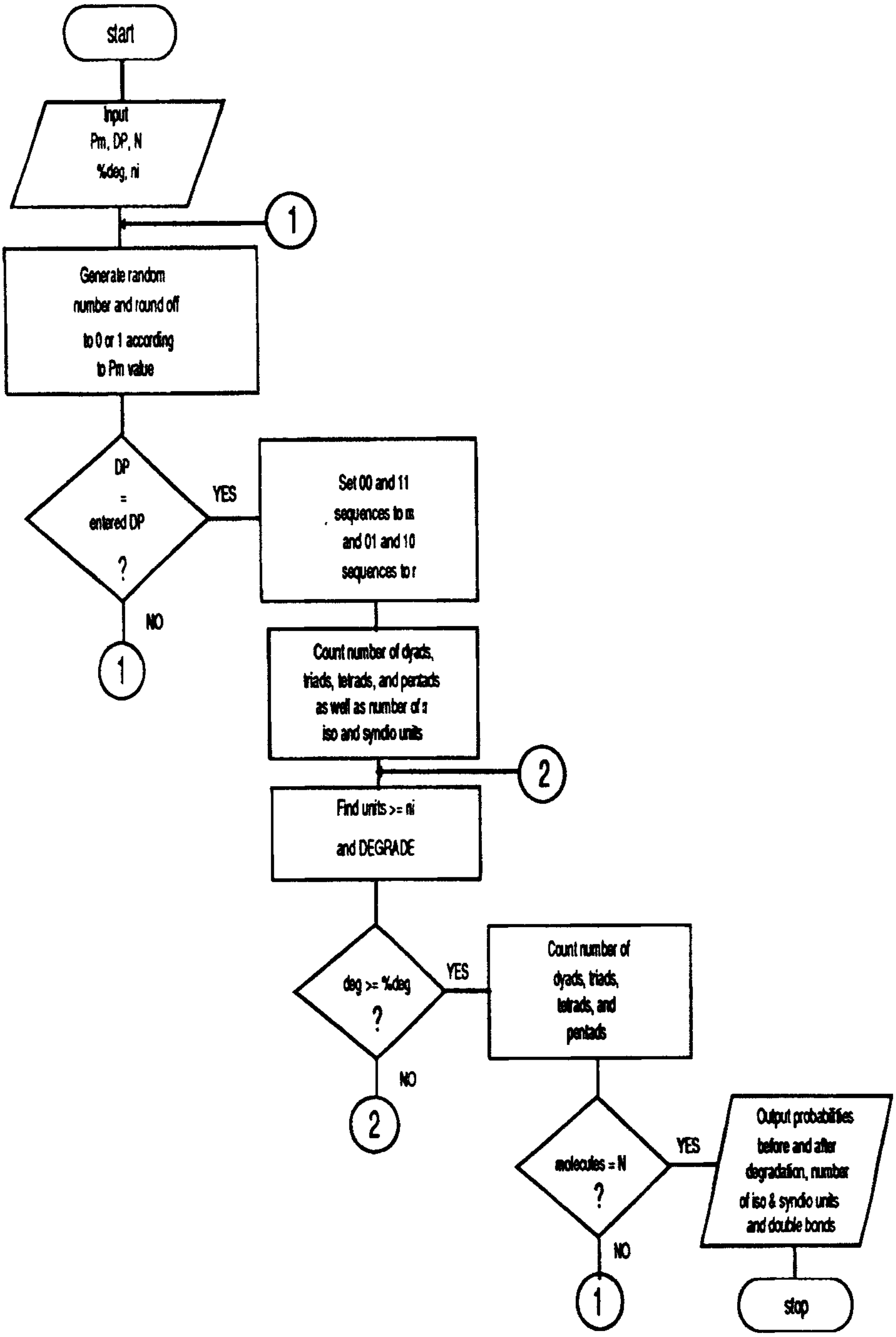


FIG. 4. Illustration of the computer program structure by means of a flowchart.

distinguishable triads, tetrads, and pentads are counted as well as the number of double bonds containing exactly $n_=$ repeat units.

The program continues to create more polymer chains until the specified number of molecules have been generated. The summations of all dyad and distinguishable triad, tetrad, and pentad sequences are then passed to procedure AVERAGE_PROBABILITIES which calculates and prints out the average values (or relative frequencies) of the appropriate stereosequences before and after degradation. The total number of isotactic, syndiotactic, and double bond sequences containing exactly n repeat units are then printed out.

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REFERENCES AND NOTES

[1] Z. Mayer, *J. Macromol. Sci.—Rev. Macromol. Chem., C10,* 263 (1964).
[2] G. Ayrey, B. Head, and R. Poller, *J. Polym. Sci., Macromol. Rev., 8,* 1 (1974).
[3] E. D. Owen, *ACS Symp. Ser., 25,* 208 (1975).
[4] C. David, *Compr. Chem. Kinet., 14,* 78 (1975).
[5] D. Braun, in *Degradation and Stabilization of Polymers* (G. Geuskens, Ed.), (Proc. Plenary Main Lect. Int. Symp., 1974), Wiley, New York, NY, 1975, p. 187.
[6] W. H. Starnes Jr., in *Developments in Polymer Degradation—3* (N. Grassie, Ed.), Applied Science Publishers, London, 1981, p. 135.
[7] G. C. Marks, J. L. Benton, and C. M. Thomas, *SCI Monogr., 26,* 204 (1967).
[8] D. E. Winkler, *J. Polym. Sci., 35,* 3 (1959).
[9] R. Stromberg, S. Straus, and B. Achhammer, *Ibid., 35,* 355 (1959).
[10] D. Braun, in *Developments in Polymer Degradation—3* (N. Grassie, Ed.), Applied Science Publishers, London, 1981, p. 101.
[11] T. Hjertberg and E. M. Sörvik, in *Degradation and Stabilization of PVC* (E. D. Owen, Ed.), Elsevier Applied Science, London, 1984, p. 21.
[12] N. Bensemra, T. van Hoang, and A. Guyot, *Polym. Degrad. Stab., 28,* 173 (1990).
[13] T. Hjertberg and E. M. Sörvik, *Polymer, 24,* 673 (1983).
[14] T. Hjertberg and E. M. Sörvik, *Ibid., 24,* 685 (1983).
[15] T. Hjertberg and E. M. Sörvik, in *Polymer Stabilization and Degradation* (P. P. Klemchuk, Ed.), (ACS Symp. Series 280), American Chemical Society, Washington, D.C., 1985, p. 259.
[16] K. S. Minsker, V. V. Lisitsky, S. V. Kolesov, and G. E. Zaikov, *J. Macromol. Sci.—Rev. Macromol. Chem., C20,* 243 (1981).

[17] A. R. Amer and J. S. Shapiro, *J. Macromol. Sci.–Chem.*, *A14*, 185 (1980).

[18] W. H. Starnes Jr., R. C. Haddon, I. M. Plitz, D. C. Hische, C. L. Schosser, F. C. Schilling, and D. Freed, *J. Polym. Prepr.*, *21*, 138 (1980).

[19] K. S. Minsker, V. V. Lisitskii, and G. E. Zaikov, *Vysokomol. Soedin, A23*, 483 (1981); *Polym. Sci. USSR, 23*, 535 (1981).

[20] B. Iván, J. P. Kennedy, T. Kelen, F. Tüdõs, T. T. Nagy, and B. Turcsányi, *J. Polym. Sci., Polym. Chem. Ed.*, *21*, 2177 (1983).

[21] J. Millán, M. Carranza, and J. Guzman, *J. Polym. Sci., Polym. Symp.*, *42*, 1411 (1973).

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

[23] J. Millán, G. Martinez, and C. Mijangos, *J. Polym. Sci., Polym. Chem. Ed.*, *18*, 506 (1980).

[24] J. Millán, G. Martinez, and C. Mijangos, *Polym. Bull.*, *5*, 407 (1981).

[25] G. Martinez, C. Mijangos, and J. Millán, *J. Macromol. Sci.–Chem.*, *A17*, 1129 (1982).

[26] G. Martinez, C. Mijangos, and J. Millán, *J. Appl. Polym. Sci.*, *28*, 33 (1983).

[27] G. Martinez, C. Mijangos, and J. Millán, *Ibid.*, *29*, 1735 (1984).

[28] G. Martinez, C. Mijangos, J. Millán, D. L. Gerrard, and W. F. Maddams, *Makromol. Chem.*, *185*, 1277 (1984).

[29] G. Martinez, C. Mijangos, and J. Millán, *Eur. Polym. J.*, *21*, 387 (1985).

[30] G. Martinez, C. Mijangos, and J. Millán, *J. Polym. Bull.*, *13*, 151 (1985).

[31] J. Millán, G. Martinez, C. Mijangos, and J. M. Gómez-Elvira, *Makromol. Chem., Macromol. Symp.*, *29*, 185 (1989).

[32] J. Millán, G. Martinez, M. L. Jimeno, P. Tieblo, C. Mijangos, and J. M. Gómez-Elvira, *Ibid.*, *48/49*, 403 (1991).

[33] G. Martinez, J. M. Gómez-Elvira, and J. Millán, *Polym. Degrad. Stab.*, *40*, 1 (1993).

[34] J. Millán, G. Martinez, and C. Mijangos, *J. Polym. Sci., Polym. Chem. Ed.*, *23*, 1077 (1985).

[35] G. Martinez, C. Mijangos, P. Terroba, and J. Millán, *Ibid.*, *26*, 1629 (1988).

[36] J. Millán, Paper presented at the 33rd IUPAC International Symposium on Macromolecules, Montreal, Canada, 1990.

[37] J. Millán, G. Martinez, J. M. Gómez-Elvira, N. Guarrotxena, and P. Tiemblo, *Polymer*, *37*, 219 (1996).

[38] J. Lara, P. Ramacieri, and G. R. Brown, *J. Macromol. Sci.–Chem.*, *26*, 69 (1989).

[39] T. Radiotis, G. R. Brown, and P. Dais, *Macromolecules*, *26*, 1445 (1993).

[40] T. Radiotis and G. R. Brown, *J. Chem. Educ.*, *72*, 133 (1995).

[41] A more realistic mechanism would take into account not only the average double bond length but also the distribution of double bonds as obtained from UV experiments. In addition, the mechanism should also incorporate not only initiation at the *mmr* sequence but also random degradation due to initiation of other labile chlorines, as is well documented.

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