

THEORETICAL STUDY OF THERMAL DEHYDROCHLORINATION OF POLY(VINYL CHLORIDE) INITIATED BY TERTIARY CHLORINE GROUPINGS*Jaroslav BURDA^a and Rudolf LUKAS^b^a *Institute of Macromolecular Chemistry,**Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic*^b *LUKAS Research,**Doubravinova 1/219, 163 04 Prague 6, Czech Republic*

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Thermal dehydrochlorination of syndiotactic poly(vinyl chloride) sequences initiated by structural defects possessing chlorine atoms bound on tertiary carbon atoms (branched structures) was theoretically studied on the low-molecular-weight models using the semiempirical quantum chemical methods MNDO and AM1. The results are compared with those obtained previously by studying the dehydrochlorination in syndiotactic sequences without defects. It was found that elimination of the first HCl molecule is much easier in the branched structure. However, this effect fast decreases with dehydrochlorination continuing along the chain due to its distinct localization in the closest vicinity of tertiary carbon atom. A detailed evaluation of possible radical and ionic intermediates revealed that for ionic mechanism of dehydrochlorination the effect of branching is perceptible slightly longer.

It is well established fact that the low thermal stability of poly(vinyl chloride) (PVC) is caused by the presence of structural defects in regular polymer chains. Allylic chlorine groups, structures possessing chlorine atom bound to the tertiary carbon atom, i.e., at the branching sites, and β -chloroaldehyde or β,β' -dichloro-ketone groupings are the structural irregularities most frequently considered as weak points in PVC chains. It was experimentally proved¹ that all these defects can be formed during vinyl chloride polymerizations. The dehydrochlorination experiments examining PVC samples enriched in the defects unambiguously confirmed¹ that these irregular structures lower the thermal stability of PVC by acting as the initiation sites of dehydrochlorination.

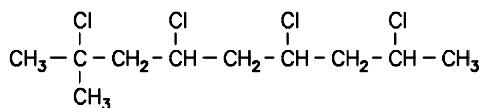
In spite of the recent progress, a deeper analysis of the course of dehydrochlorination is inaccessible because the experimental data so far obtained do not provide all information needed. Since a better understanding of the dehydrochlorination process is a

* Part V in the series Thermal Dehydrochlorination of Poly(vinyl chloride); Part IV: see ref.³.

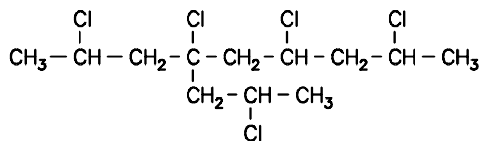
crucial point for a further development in this area, we tried to apply a theoretical approach based on the computer experiments simulating a real dehydrochlorination process^{2,3}. Low-molecular-weight oligomers were chosen as model structures and the semiempirical quantum chemical methods MNDO and AM1 were employed to perform the calculations. The simulation of the overall dehydrochlorination process was carried out at two levels which helps to compare (i) the properties of various unsaturated products from individual dehydrochlorination steps and (ii) the changes in properties of radical and ionic intermediates, i.e., of the structures formed by the detachment of chlorine particle. The results obtained in the study of a stepwise dehydrochlorination of linear vinyl chloride oligomers, including the explanation of the activation effect of allylic and polyene structures, were already published^{2,3}. This work is a continuation of the study and deals with the evaluation of dehydrochlorination behaviour of PVC sequences, which contain branched structures possessing chlorine atoms bound to the tertiary carbon atoms at branching sites.

CALCULATIONS

To reach compatibility of the results with those previously published for the linear PVC models^{2,3}, the same semiempirical quantum chemical methods, MNDO and AM1, were used in this study. Vinyl chloride tetramer models in trans-trans syndiotactic arrangement were chosen as the model structures because it was found^{2,3} that these systems are sufficiently large for the description of the dehydrochlorination process. The basic effect of branching was simulated by methyl group bound to the second carbon atom in 2-methyl-2,4,6,8-tetrachlorononane (*I*). The effect of a longer branch was examined using 2-chloropropyl substituent on the fourth carbon atom in 4-(2-chloropropyl)-2,4,6,8-tetrachlorononane (*II*). In this case, elimination of only one HCl molecule was evaluated by AM1 method.



I



II

The calculations of the models were run in the same way as previously^{2,3}: their geometries were fully optimized, the formation of conjugated π -electron system starting from the second carbon atom was simulated and the dehydrochlorination was followed until the third double bond was formed. Each dehydrochlorination step started by the detachment of a chlorine particle, either in the form of radical or anion, and then hydrogen was detached under the formation of HCl and an unsaturated product. Repeating these steps was used to find the effect of substitution at the edge of π -electron system on the allylic and polyene activation of the propagating dehydrochlorination.

RESULTS AND DISCUSSION

Denoting² the HCl elimination as the process $A(R \rightarrow R' + \text{HCl})$ and the detachments of Cl^\bullet and Cl^- as the partial steps B and B' , respectively ($R \rightarrow R'' + \text{Cl}^x$, $x = \bullet$ or $-$), Table I shows the energy balances of all the processes investigated. It is apparent that, from the point of view of energy, the easiest is the first HCl elimination and the first detachment of chlorine particle, i.e., from the saturated structure. If we compare these (AM1) values with those calculated for the corresponding non-branched structure² (-0.001 vs -0.235 eV, $\Delta(\Delta E_A) = 22.58$ kJ/mol; 2.88 vs 2.58 eV, $\Delta(\Delta E_B) = 28.95$ kJ/mol; 7.20 vs 6.47 eV, $\Delta(\Delta E_{B'}) = 70.42$ kJ/mol) it can be concluded that the chlorine atom bound at the branching site is less stable than the chlorine atoms in regular structure units of PVC. It is also obvious from the last line in Table I that the tendency for the formation of sp^2 hybridized tertiary carbon atom increases with increasing length of the side chain [$\Delta E(II) - \Delta E(I) = -28.53$ kJ/mol (process A); -24.98 kJ/mol (process B); -8.70 kJ/mol (process B')]. However, the formation and extension of the conjugated π -electron sys-

TABLE I
Energetical balances (eV) of the HCl elimination (A) and Cl^\bullet (B) and Cl^- detachment (B') from branched structures I and II and their unsaturated derivatives

Reaction step ^a	ΔE_A		ΔE_B		$\Delta E_{B'}$	
	MNDO	AM1	MNDO	AM1	MNDO	AM1
$I \rightarrow I(3 \text{ Cl})$	0.181	-0.235	2.130	2.58	6.01	6.47
$I(3 \text{ Cl}) \rightarrow I(2 \text{ Cl})$	0.505	-0.101	2.466	2.61	5.33	6.03
$I(2 \text{ Cl}) \rightarrow I(1 \text{ Cl})$	0.560	-0.094	2.521	2.61	5.10	5.68
$II(5 \text{ Cl}) \rightarrow II(4 \text{ Cl})$	-	-0.531	-	2.321	-	6.378

^a $I(n \text{ Cl}) \rightarrow II(n - 1 \text{ Cl})$ means dehydrochlorination or dechlorination reaction of the unsaturated structure with n Cl atoms to that with $(n - 1)$ Cl atoms.

For $\text{H} + \text{Cl} \rightarrow \text{HCl}$, $\Delta E = -403.1$ kJ/mol (MNDO), -493.3 kJ/mol (AM1) and -386.2 ± 0.4 kJ/mol (experimental value⁴)

tem cause a fast convergence of the values to those found for the similar but linear syndiotactic model²: $\Delta(\Delta E_A(2 \text{ Cl} \rightarrow 1 \text{ Cl}))$, 0.00 kJ/mol for MNDO and 0.04 kJ/mol for AM1. These results lead to the conclusion that from the point of view of energy the presence of branched structures with chlorine atoms bound at the branching sites strongly lower the thermal stability of PVC. Their adverse effect increases with the increasing branch length, and especially dominates in the initiation phase of dehydrochlorination.

Several interesting dependences can be found if we compare the energy balances of products from various degrees of dehydrochlorination: Thus, on the basis of the results in Table I, one can observe that the value of activation energy of dehydrochlorination proceeding by the radical mechanism, ΔE_B , is in the first reaction step (the detachment of chlorine particle from the tertiary carbon atom) distinctly lower in comparison with the non-branched model. After detachment of the next chlorine atom, however, the differences between branched and linear models are smaller and eventually, after several dehydrochlorination steps, negligible. Further, in contrast to the linear model, the energies in branched structures increase (in AM1 results only slightly) with the decreasing number of residual chlorine atoms (the process is spontaneous only due to the entropic pattern of Gibbs energy). However, the increasing polyene system causes the energies to converge to the same values in both cases.

Similarly, the energies of ionic intermediates in branched models ΔE_B , are also lower. However, the differences are more pronounced in comparison with the radical reactions, and also the ratio of the energies branched/linear models converges with the increasing π -electron system to unity considerably more slowly.

The eigenvalues of the frontier orbitals, HOMO and LUMO, of the basic systems given in Table II resemble those presented previously². It is rather difficult to predict from these values a kinetic behaviour, but it might be stated that the effect of the tacticity of polymer chain (syndio or iso) is stronger than the effect of branching. The AM1 method gives the values of HOMO energies a little higher for the systems with tertiary carbon atoms, especially in the case of the structure with one double bond; this may indicate a slightly faster course of dehydrochlorination in this stage of the reaction. The HOMO and LUMO eigenvalues of the model with 2-chloropropyl side chain (*II*) suggest the same tendency.

The values of the frontier orbital energies of radical intermediates, HDOMO (Highest Double Occupied Molecular Orbital), SOMO and LUMO are practically the same for both the linear² and branched models (Table II). Here, an interesting effect of the side chain length can be observed. The SOMO energy of the structure *II* is relatively very low and it indicates a slower transition via such a radical than might be assumed for the structure *I*.

Unlike in the homolytic mechanism, the values of LUMO energies of branched cationic intermediates (after chlorine anion detachment) are significantly higher than

those found for the linear model (Table II). Therefore, under the assumption of ionic mechanism, it can be predicted that the dehydrochlorination proceeds faster in the branched structures. As far as the type of the frontier orbitals is concerned, it may be stated that the discussion and conclusions previously drawn for the linear models² remain valid. In spite of the fact that the absolute values of energies obtained by the MNDO and AM1 methods differ substantially, the observed trends are qualitatively the same.

The analysis of the driving force of dehydrochlorination, based on the evaluation of electron charge distributions, gives the same information about the nature of allylic and polyene activation, as previously published^{2,3} for linear models. Hence, these results give a further support to the idea that the dehydrochlorination process does not proceed by a generally accepted zip mechanism and suggest its replacement by the "polyene alternation growth" mechanism^{2,3,5}.

A detailed comparison of the electron charge distributions allows the effect of branching to be investigated and understood. It is clear from Fig. 1 that the branching

TABLE II
Frontier orbital energies (eV) of branched structures *I* and *II*, their unsaturated derivatives and their radical and cationic intermediates

Structure	MNDO	AM1	AM1 ^a
		HOMO/LUMO	
<i>I</i>	-12.04/0.33	-12.92/0.93	-10.98/0/87
<i>I</i> (3 Cl)	-10.09/-0.10	-9.68/0.24	-10.13/0.29
<i>I</i> (2 Cl)	-9.33/-0.39	-8.92/-0.11	-9.13/-0.33
<i>I</i> (1 Cl)	-8.85/-0.60	-8.48/-0.44	-8.64/-0.43
<i>II</i>	-	-10.87/0.99	-
<i>II</i> (4 Cl)	-	-9.98/0.37	-
Radicals		HDOMO/SOMO/LUMO	
<i>I</i> (3 Cl)	-12.06/-4.54/0.36	-11.08/-3.91/1.12	-11.11/-4.04/1.12
<i>I</i> (2 Cl)	-10.52/-4.51/0.54	-10.33/-4.11/1.24	-10.59/-4.19/1.22
<i>I</i> (1 Cl)	-9.57/-4.46/0.47	-9.37/-4.18/0.76	-9.60/-4.25/0.78
<i>II</i> (4 Cl)	-	-10.88/-4.26/1.22	-
Cations		HOMO/LUMO	
<i>I</i> (3 Cl)	-14.10/-7.85	-13.23/-7.09	-12.94/-7.76
<i>I</i> (2 Cl)	-14.46/-7.25	-13.39/-6.85	-13.30/-7.13
<i>I</i> (1 Cl)	-14.15/-6.80	-13.60/-6.46	-13.72/-6.67
<i>II</i> (4 Cl)	-	-13.64/-7.27	-

^a Unpublished values for the corresponding linear structures.

together with the presence of electronegative chlorine atoms shift distinctly the partial charge on the tertiary carbon atom to the positive values (AM1 results). The MNDO results suggest that these effects compensate each other and as a result the positive charge on the carbon atom is lowered. Nevertheless, after detachment of the first chlorine particle, the distribution of electron density is practically identical with that found for the linear systems. To decide which method, MNDO or AM1, gives more reliable electron charge distributions, we carried out the *ab initio* calculations using 2-chloropropane and 2-chloro-2-methylpropane. The calculations proceeded in the valence triple zeta base with polarization functions (TZP) and revealed that the AM1 method gives qualitatively and also quantitatively more correct values of partial charges. Therefore, it can be concluded that the partial charges of the linear and branched chains differ only in the closest vicinity of the tertiary carbon atom. Thus, the branching can be considered as a small perturbation with respect to the linear structure which is sufficiently localized and practically disappears after the detachment of chlorine particle. The same considerations about the existence of charge potential $\mu(C^{\omega}-C^{\alpha})$, which led to the explanation of the driving force of dehydrochlorination^{2,3}, reflect here the dependence of energy balance on the length of π -electron system and

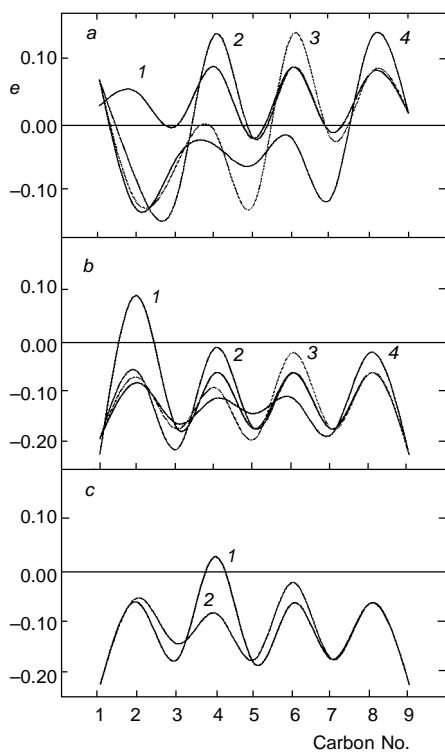


FIG. 1
Partial electron charge (e) distribution on the main chain carbon atoms in structure *I* and its unsaturated derivatives obtained by MNDO (a) and AM1 (b) methods and in structure *II* and its unsaturated derivatives obtained by AM1 method (c). 1 Saturated system, 2 system with single double bond, 3 system with two double bonds, 4 system with three double bonds

explain why the detachment of the first HCl molecule is much easier than subsequent propagation step of growing polyene sequence.

CONCLUSIONS

The theoretical investigation of PVC structural irregularities in branched models containing chlorine atoms bound to the tertiary carbon atoms confirmed the experiments, which revealed that these defects are also responsible for the low thermal stability of PVC. The simulation of individual consecutive dehydrochlorination steps and the analysis of various radical and ionic reaction intermediates revealed that the effect of branching is restricted to the closest vicinity of the tertiary carbon atoms and has a tendency to disappear quickly with the proceeding dehydrochlorination process. It may be predicted that the extent of the activation effect is dependent on the reaction mechanism of dehydrochlorination and acts farther in the case of ionic mechanism. Nevertheless, after several consecutive HCl eliminations, the dehydrochlorination behaviour of branched structures converges to that of linear sequences of PVC.

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