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ON DEHYDROCHLORINATION OF CROSSLINKED POLY(VINYL CHLORIDE)

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Abstract—Using the semiempirical quantum-chemical AM1 method, the geometries of double chain molecules of $(C_5H_{9-i}Cl_{2-i})(C_5H_{9-j}Cl_{2-j})CH–CH(C_5H_{8-m}Cl_{3-m})(C_5H_{8-n}Cl_{3-n})$ with i, j, m, n = 0–2 were optimized within the fully non-rigid model as well as with the partial influence of the environment modeled by chains planarity. Double C=C bonds are formed primarily in the vicinity of the inter-chain bond but alternatively on both chains. The results obtained for both mentioned models differ substantially.

INTRODUCTION

PVC is a widely used polymer due to its low price and favourable physical and physico-chemical properties. However, its main drawback is its low thermal stability which makes the addition of stabilizers during processing and application of the polymer inevitable. The PVC thermal degradation resides in HCl evolution accompanied with the formation of conjugated polyene sequences in the polymer chain. The polyene sequences are formed as a result of the chain reaction with a special mechanism called the zip elimination [1–3]. The most frequent length of the sequences is between 5–10 double bonds. The PVC degradation has been extensively studied [1–3]; however, despite this great effort, many aspects of the mechanism of PVC ageing remain unresolved.

Quantum chemistry calculations belong to the methods applied for years in order to get a deeper insight into the mechanism of degradation [4–13]. The isolated molecules of model compounds mimicking the PVC chain or defect structures in the chain have been subjected to the study. In all cases it has dealt with the single chain models. However, it is known that the crosslinking of polymer chains proceeds during the PVC degradation even at relatively low temperatures and becomes more important as the temperature increases. The crosslinking is known to be catalyzed by hydrogen chloride [1–3]. The cross-linked model compounds in solid state have not been studied yet although the proximity of the crosslinked chains may lead to the change of the reaction mechanism.

The termination of dehydrochlorination has not been explained satisfactorily yet. The irreversibility of the whole reaction is supposed, i.e. the split HCl is removed immediately and reaction barriers heights determine the reaction. However, this supposition is not fulfilled completely. In real PVC systems the non-vanishing portion of HCl remains absorbed in solid-state samples. The complementary treatment supposes the thermodynamic equilibrium and the reaction products are distributed according to their heats of formation. Using this treatment the existence and position of the volume changes maximum during PVC dehydrochlorination has been successfully explained [14].

The aim of this article is the theoretical study of the double bonds distribution in CPVC from the reaction kinetics. In agreement with the assumption [15] of extended syndiotactic structures we may restrict to the most probably occurring crosslinked syndiotactic chains. In such systems the four-centric 1,2-elimination of HCl is the most probable due to geometrical reasons [3].

For the sake of simplicity, we may restrict to the model consisting of two finite chains. In the first step, the inter-chain C–C bond in the central parts of the chains may be supposed. In Fig. 1 the possible positions for HCl removed in the next steps are marked by small characters. The optimal chain geometry should depend on the extent of dehydrochlorination, on the location of arising double bonds as well as on the environmental influences. The relative effects of these factors may be approximately described by the following models [14]:

(i) Fully rigid model, the dominant influence of the environment is supposed. Consequently, both chains must be planar and the planes are parallel.

(ii) Fully non-rigid model, the vanishing influence of the environment is supposed. There are no additional restrictions for chain geometries.

(iii) Intermediate model between fully rigid and fully non-rigid ones. The partial influence of the environment is modeled by chains planarity. In contrast to the fully rigid model, there are no restrictions for mutual planes orientations.

Using these model systems, the above mentioned conclusions obtained for isolated single-chain oligomers may be verified.

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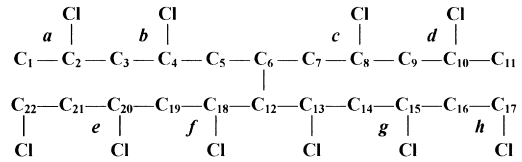

Fig. 1. Schematic numbering of carbon atoms and possible double bond positions.

METHOD

The standard semiempirical AM1 (Austin Model) method of quantum chemistry (AMPAC program package) [16, 17] has been used in order to find the optimal geometries of double chain molecule of $(C_5H_{9-i}Cl_{2-i})(C_5H_{9-j}Cl_{2-j})CH–CH(C_5H_{8-m}Cl_{3-m})(C_5H_{8-n}Cl_{3-n})$ with $i, j, m, n = 0–2$ within the models mentioned above (Fig. 2). All calculations were performed in higher precision (keyword PRECISE) using the Davidon–Fletcher–Powell optimization procedure [18, 19]. The results are evaluated in terms like heat of formation H_f of the molecule, charges Q of individual atoms and HOMO–LUMO energy separation [20]. Due to the great number of possible combinations arising by consecutive dehydrochlorination we had to restrict to the most probable ones (with minimal H_f values). It means that in the next step only the configurations arising from the lowest energy configuration in the previous step are investigated (see Table 1 and 2).

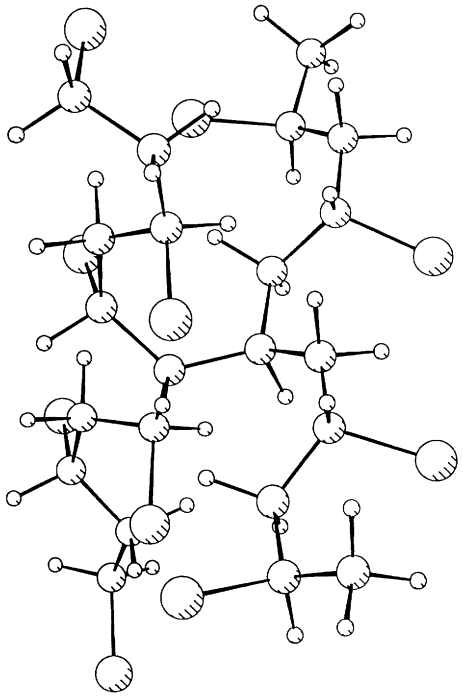

Fig. 2. Structure of $(C_5H_9Cl_2)(C_5H_9Cl_2)CH–CH(C_5H_8Cl_3)(C_5H_8Cl_3)$ (model A0).

RESULTS AND DISCUSSION

Quantum chemical calculations indicate that the fully rigid model (i) (parallel chains planes) corre-

Table 1. The heat of formation values, H_f, for the selected systems with planar chains (N: the number of double bonds, the systems with the lowest energy for every N are bold)

Model system	N	Double bonds position	H_f/kJ mol^{-1}	Model system	N	Double bonds position	H_f/kJ mol^{-1}
A0	**0**		**−533.566**	B0	0		−514.474
A1a	1	a	−384.306				
A1b	1	b	−420.564				
A1c	1	c	−442.252				
A1d	1	d	−413.949				
A1e	1	e	−419.099				
A1f	**1**	**f**	**−487.804**				
A1g	1	g	−421.066				
A1h	1	h	−366.052				
A2a	2	fa	−338.670				
A2b	2	fb	−373.881				
A2c	**2**	**fc**	**−389.959**				
A2d	2	fd	−363.665				
A2e	2	fe	−375.891				
A2g	2	fg	−362.661				
A2h	2	fh	−320.834				
A3a	3	fca	−241.118				
A3b	3	fcb	−264.606				
A3d	3	fcd	−267.620				
A3e	**3**	**fce**	**−278.673**				
A3g	3	fcg	−262.345				
A3h	3	fch	−222.445				
A4a	4	fcea	−129.205				
A4b	4	fceb	−153.949				
A4d	**4**	**fced**	**−157.340**				
A4g	4	fceg	−152.734				
A4h	4	fceh	−111.160				
A5a	5	fceda	−7.201				
A5b	**5**	**fcedb**	**−32.908**				
A5g	5	fcedg	−23.237				
A5h	5	fcedh	10.341				
A8	**8**	**abcdefgh**	**406.203**	B8	8	abcdefgh	410.013

Table 2. The heat of formation values, H_f, for the selected systems with non-planar chains (N: number of double bonds, the systems with the lowest energy for every N are bold)

Model system	N	Double bonds position	H_f/kJ mol^{-1}	Model system	N	Double bonds position	H_f/kJ mol^{-1}
C0	**0**		**−816.384**	D0	0		−816.217
C1a	1	a	−659.588	D1a	1	a	−657.621
C1b	1	b	−654.481	D1b	1	b	−664.026
C1c	1	c	−669.386	**D1c**	**1**	**c**	**−685.002**
C1d	1	d	−665.450	D1d	1	d	−663.650
C1e	1	e	−660.342	D1e	1	e	−673.991
C1f	**1**	**f**	**−693.334**	D1f	1	f	−677.717
C1g	1	g	−678.303	D1g	1	g	−681.234
C1h	1	h	−647.111	D1h	1	h	−644.516
C2a	2	fa	−536.455				
C2b	2	fb	−544.493				
C2c	2	fc	−551.025				
C2d	2	fd	−548.931				
C2e	**2**	**fe**	**−559.440**				
C2g	**2**	**fg**	**−559.691**				
C2h	2	fh	−536.748				
C3a	3	fga	−402.519	C'3a	3	fea	−402.938
C3b	3	fgb	−410.976	C'3b	3	feb	−417.885
C3c	3	fgc	−416.126	C'3c	3	fec	−416.963
C3d	3	fgd	−414.870	C'3d	3	fed	−415.624
C3e	**3**	**fge**	**−424.290**	**C'3g**	**3**	**feg**	**−424.290**
C3h	3	fgh	−399.630	C'3h	3	feh	−395.778
C4a	4	fgea	−267.411				
C4b	4	fgeb	−275.994				
C4c	**4**	**fgec**	**−281.479**				
C4d	4	fged	−279.301				
C4h	4	fgeh	−264.187				
C5a	5	fgeca	−123.971				
C5b	5	fgecb	−136.155				
C5d	**5**	**fgecd**	**−140.090**				
C5h	5	fgech	−121.250				
C8	**8**	**abcdefgh**	**316.690**	D8	8	abcdefgh	322.166

sponds to unstable systems because of missing inter-chain C_6–C_{12} bonds. Consequently, only the intermediate model (iii) with non-parallel chains planes may be suitable for the solid-state effects imitation. The dependence of the energy on the inter-chain angle δ exhibits two minima. For the sake of clarity let us denote the corresponding model systems with starting inter-chain angles (before geometry optimization) $\delta > 90^\circ$ and $\delta < 90^\circ$ as A and B (see Table 1).

The fully non-rigid model (ii) corresponds to isolated systems in vacuum. Its results will be presented for comparison only. In analogy with the facts mentioned above we may denote as C and D the model systems with starting inter-chain angles $\delta > 90^\circ$ and $\delta < 90^\circ$, respectively (see Table 2).

Tables 1 and 2 describe the dependence of H_f values of the systems under study on the position of the latest double bond created by HCl split. These data indicate the relative stability of individual double bond isomers within the same number of double bonds. It is evident that B (solid state) models are more stable than A ones (compare A0

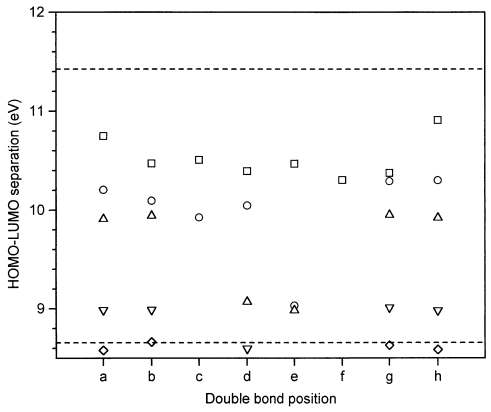

Fig. 3. The values of HOMO–LUMO separation for the systems B1x (squares), B2x (circles), B3x (up triangles), B4x (down triangles) and B5x (diamonds) for x = a–h (see Table 1). The dashed lines correspond to B0 (upper) and B8 (down) systems.

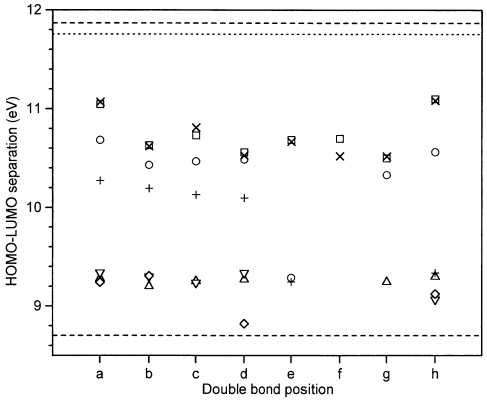

Fig. 4. The values of HOMO–LUMO separation for the systems C1x (squares), D1x (×), C2x (circles), C3x (up triangles), C′3x (+), C4x (down triangles) and C5x (diamonds) for x = a–h (see Table 2). The dotted line corresponds to D0, the dashed lines correspond to C0 (upper) and C8 (down) systems.

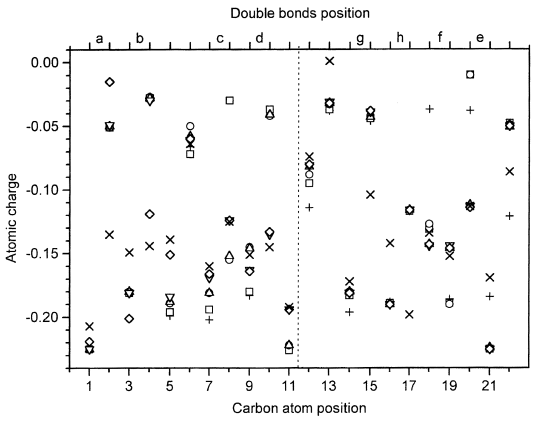

Fig. 5. Carbon atom charges for the systems B0 (+), B1f (squares), B2c (circles), B3e (up triangles), B4d (down triangles), B5b (diamonds) and B8 (×). The dotted line separates the areas corresponding to individual chains (for carbon atom numbering and double bonds positions see Fig. 1).

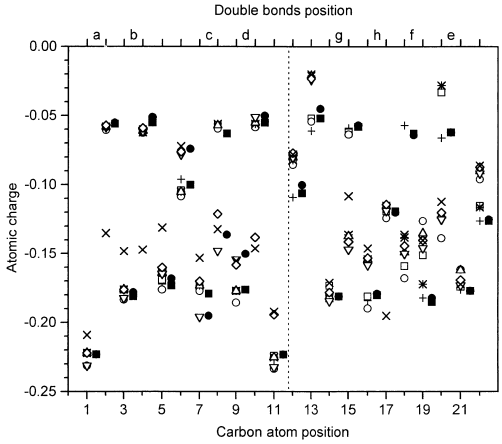

Fig. 6. Carbon atom charges for the systems C0 (+crosses), D0 (full squares), C1f (open squares), D1c (full circles), C2e (open circles), C2g (asterisks), C3e (up triangles), C4c (down triangles), C5d (diamonds) and C8 (×). The dotted line separates the areas corresponding to individual chains (for carbon atom numbering and double bonds positions see Fig. 1). For better understanding the symbols for D0 and D1c systems are shifted right.

and B0 as well as A8 and B8 model systems, respectively). Consequently, the remaining B model systems are not presented in this study. More complicated situation is with non-rigid C and D (in vacuum) model systems. As D0 system is only by 0.1 kJ mol^{-1} less stable than C0 one, the D1x (x = a–h) systems are presented, too. However, these are less stable than analogous C1x (x = a–h) ones. Consequently, the D2x (x = a–h) systems are not presented. Analogously, C2e model system is only by 0.4 kJ mol^{-1} less stable than the optimal C2g one and so the C′3x (x = a–h) series originating in C2e is presented, too. Fortunately, the optimal model systems C′3g and C3e are identical and produce the common C4x (x = a–h) series.

In agreement with [3, 12], our results confirm that double C=C bonds are created in conjugated sequences primarily in the vicinity of the inter-chain C_6–C_{12} bond but alternating on both chains. This is in agreement with generalized "alternation growth" mechanism [12]. These sequences, however, are different for isolated molecules and for the systems taking into account the simple solid state effects (compare Tables 1 and 2). Consequently, the results on the dehydrochlorination of isolated oligomers may not be reliable when applying to CPVC systems and the solid-state influence is to be accounted for.

Figures 3 and 4 represent the dependence of HOMO–LUMO separation values of the above mentioned systems (see Tables 1 and 2) on the position of the latest double bond formed by HCl elimination. It is evident that not in all cases the minimal HOMO–LUMO separation corresponds to the most stable system within the series of model systems with the same number of double bonds. This supposition may be only partially verified [12].

Atomic charges on individual carbon atoms (for atoms numbering see Fig. 1) for the most stable systems within the series with the same number of double bonds (compare the underlined systems in Tables 1 and 2) are presented in Figs 5 and 6. It is evident that the charges on carbons bonded to chlorine are less negative than the remaining ones. Substantial changes in atomic charges are caused by the dehydrochlorination and are located prevailingly in the neighbourhood of the double bond formed. The hypothesis on the preferential dehydrochlorination in the direction of maximal charge potential $\mu(C^{\omega}–C^{\alpha})$ [12] cannot be confirmed. According to this hypothesis the dehydrochlorination in our systems should proceed exclusively in the same chain as the charges on their end atoms remain practically constant in comparison with the charge difference between end carbon atoms bonded to Cl (positions 17 and 22 of the 2nd chain) and H (positions 1 and 11 of the 1st chain) atoms.

Here, it must be mentioned that the ending methyl groups are not equivalent to the methylenes in a chain. The influence of this distinction on energy parameters decreases with the chain length and the calculations carried out using variously extensive systems indicate that sufficiently exact results can be achieved already with C_7 systems [12, 13]. However, this non-equivalence is preserved in electronic structure parameters and so only their trends may be deduced from our calculations.

Finally, it may be concluded that there are significant differences between the results obtained for single-chain and crosslinked double-chain molecules as well as between the isolated systems and those accounting the solid-state effects (at least qualitatively). The results on energetic parameters like H_f cannot be equivalently substituted by analogous ones based on atomic charges or HOMO–LUMO orbitals. Structural changes accompanying the dehydrochlorination are significant and cannot be neglected. Nevertheless, more detailed theoretical studies involving more sophisticated models of solid-state influences would be desirable.

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