Pathway for polymerization of *p*-xylylenes

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The pathway for polymerization of *p*-xylylenes is analysed at a theoretical level. The influence of the substituents on the aromatic ring on the conditions of the reaction is discussed on the basis of the Taft and Topson rules and Δq_π constants.

(Keywords: polymerization pathway; polyxylylenes; modelling)

INTRODUCTION

Pyrolytic polymerization of *p*-xylylenes during deposition of the monomer from the gas phase onto different substrates is of special interest, particularly for waterproof and dielectric coatings in microelectronics[1]. Cyclic dimers of *p*-xylylenes with different kinds of substituents (*p*-cyclophanes) are used in this synthesis as starting materials. On passing through the pyrolytic zone, the starting cyclophane is converted into the corresponding substituted *p*-xylylene (see *Figure 1*), which then polymerizes on the substrate[1].

It has been shown that the morphology of the polymer film and its properties depend very strongly on the substrate temperature and pyrolytic conditions[2,3]. However, the correct set of conditions for producing the polymers depends on the nature of the starting material (what kind of substituted cyclophane is used).

In spite of wide industrial application of pyrolytic polymerization of *p*-xylylenes, there are only a few data concerning the mechanism of this process[4]. The fact that no solvents nor catalysts take part in the pyrolytic polymerization of cyclophanes makes this process very interesting not only from an industrial but also from a theoretical point of view.

In the present paper we have studied the theoretical behaviour of [2.2]-*p*-cyclophane and its derivatives during the polymerization process. The aim of our calculation is to understand better the mechanism of polymerization of these molecules and to establish the influence of various substituents on the aromatic ring both on the decomposition of the cyclophane molecule in the pyrolytic zone and on the polymerization process.

Three types of cyclophanes are considered in this work: unsubstituted [2.2]-*p*-cyclophane, chloro-*p*-cyclophane and cyano-*p*-cyclophane. The first two are used in commercial production of polymer films (their commercial names are Parylen N and C). Cyano-*p*-cyclophane does not have industrial application, but there are data[5] showing that introduction of the CN group in the aromatic rings of cyclophanes changes the properties of the obtained polymer dramatically. Therefore, theoretical investigation of the influence of the CN group on the characteristics of the pyrolytic polymerization process is of interest.

METHODOLOGY

All calculations were performed using the AM1[6] (Austin model 1) method from MOPAC software[7] included in the Cerius package[8], with total optimization of the geometry using the BFGS algorithm and proving the absolute minima with the EF (eigenvector-following) facility. Initial geometries were obtained by the Molecular Mechanics method[9] from the same software package. The positions of the substituents in the aromatic rings were fixed as *ortho* to the bridge following the cyclophane species.

RESULTS AND DISCUSSION

The chemical scheme of pyrolytic synthesis of poly(*p*-xylylenes) is shown in *Figure 1*. The mechanism of thermal decomposition of cyclophanes in the pyrolytic zone with the cleavage of the two CH–CH bonds in the molecule and the formation of the intermediate quinoid structure has been studied extensively[10]. However, in a few cases, when the starting material is substituted, cleavage of only one CH–CH bond takes place and other intermediates are formed[11]. This fact may be considered as an exception to the common rule[12], but it shows the very important role of the substituent in the benzene ring and the possibility that this can change the mechanism of polymerization.

The intermediate formed can be a tetraolefin or a biradical, as shown in *Figure 2*. The olefin is the preferred structure[13], and our calculation gives evidence for this, since the overlap population of the side bonds shows the typical character of a double bond. Additionally, we performed the corresponding calculation for the biradical with triplet multiplicity and the results show that this

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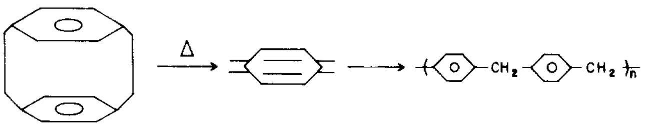

Figure 1 Reaction for the polymerization of *p*-xylylenes in pyrolytic pathway

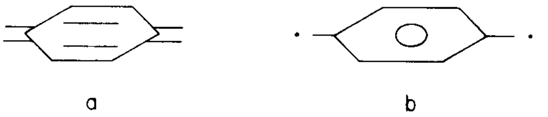

Figure 2 *p*-Quinodimethane in (a) tetraolefin form and (b) biradical form

Table 1 Relevant calculated data

Compound	ΔH_f (kcal mol^{-1})	Total energy (eV)	Ionization potential (eV)
Cyclophane	60.03	−2267.507	8.742
CN-cyclophane	124.109	−2098.485	9.41
Cl-cyclophane	47.09	−2987.67	8.997
p-Quinodimethane[a]	59.93 (56.1)	−1132.456	8.25 (8.18)
CN-*p*-quinodimethane	92.25	−1452.93	8.62
Cl-*p*-quinodimethane	53.75	−1492.52	8.41
p-Quinodimethane	81.705	−1131.526	–

[a] The values in parentheses correspond to those reported by Dewar[14]

structure is possible because the energetic difference between the olefin and the biradical is only 21.45 kcal mol^{-1}. Such a small energetic difference between structures is the reason for the very high reactivity of the *p*-xylylene molecule, since it is possible to reach this structure.

Dewar[14] carried out a similar theoretical study of the spectroscopic behaviour of *p*-quinodimethane (*Figure 2a*). In that paper Dewar reports a calculation using the MNDO (modified neglect of differential overlap) method with interesting results that we use for comparison since one method used in this paper (AM1) is of the same family.

Relevant results including the main ones of Dewar are shown in *Table 1*. The comparison between our results and those of Dewar's work are in good agreement.

We start our study by analysing the nature of the chemical behaviour of the cyclophane molecule without substituents, which corresponds to the D_{2h} point group, as well as its product *p*-quinodimethane. The frontier orbitals for both species are shown in *Figure 3*.

The relevant feature in this diagram is that the HOMO (highest occupied molecular orbital) of the *p*-quinodimethane b_{1u} arises from the LUMO (lowest unoccupied molecular orbital) of the cyclophane, and in the same sense the HOMO b_{2g} of cyclophane generates the LUMO of *p*-quinodimethane. In both cases we have concentrated on the most important molecular orbitals (MOs) for the second molecule, since we expect that the first MO will participate in the polymerization reaction as a nucleophilic agent and the second will be a receptor of charge as an electrophilic reagent. Furthermore, this second orbital is lower in energy by almost 1 eV than the LUMO of the cyclophane and it will thus be more accessible for electronic attack. These orbitals will be cited for all the molecules we have studied, although the group symmetry changes when we have a substituent on the aromatic ring.

The size of the atomic orbitals that contribute to the molecular orbitals corresponds in a rough way to their respective amounts in each case, as shown in *Figure 3*. In this sense we can see that the p_z atomic orbitals of π delocalization for both *para* substitution positions have the biggest contribution. The complete molecular orbital participates in the polymerization reaction, but we expect that the reaction would take place on the p_z orbitals. The phenomenon is present in both the HOMO and the LUMO cases.

The HOMO-1 MO b_{3u} for cyclophane is an additional interesting pathway for the generation of *p*-quinodimethane since it includes p_z atomic orbitals that are not present in b_{2g}; the difference between this orbital and the HOMO is only 0.63 eV.

All the *p*-quinodimethane derivatives present the same shape of frontier orbitals and all would correspond to the same irreducible representation (HOMO b_{1u} and LUMO b_{2g}) if the symmetry were the same for all of them. This behaviour is present in spite of the attached radical because these substituents do not take any part in the reactions. Their main influence is in the changes of the behaviour of each species. It is therefore expected that all of them should follow the same polymerization mechanism. Indeed, this occurs because polymers of all of the variations exist, but the polymerization reactions are easier and more effective depending on the substituent. Thus, the analysis of the influence of the substituent is very important.

The main effects to consider are the field and the resonance effects, which change the behaviour of the aromatic ring in cyclophane, because these are classified as long-range effects[15]. Then we can make an interesting analysis taking advantage of the Taft and Topson parameters[15] and the Δq_π[15].

If H is considered as a neutral species, the CN is classified as an electron-withdrawing group[15] and Cl

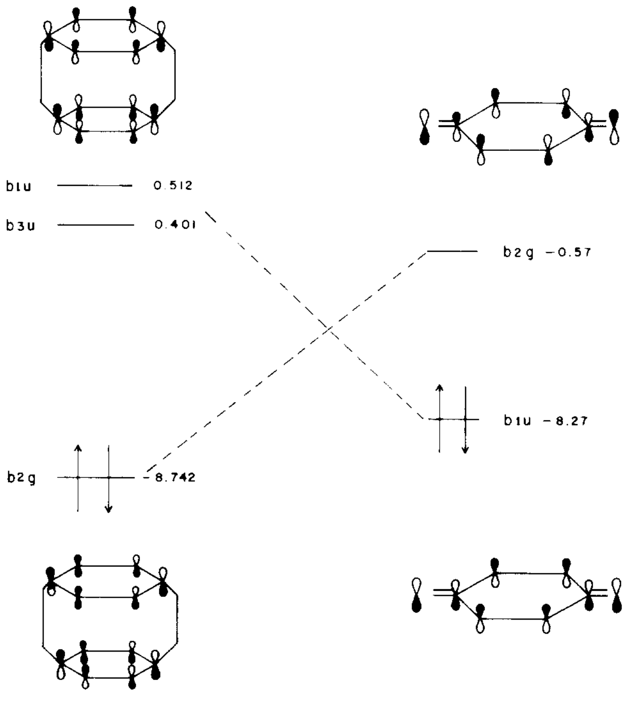

Figure 3 Frontier orbitals for cyclophane and *p*-quinodimethane

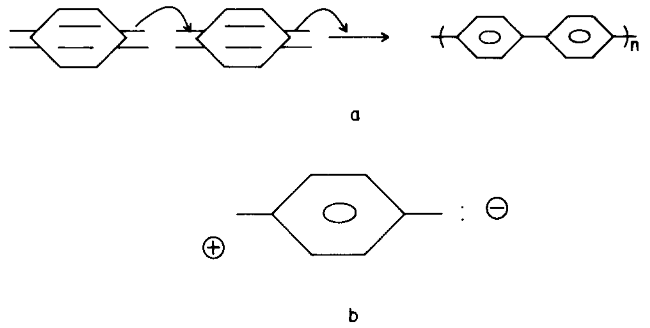

Figure 4 (a) Concatenation of tetraolefins to yield poly(*p*-xylylene). (b) Polarized form of tetraolefin

substituted in a ring as an electron-donating group[15]. However, in the case of the chloride substituent, deactivation of the electrophilic substitution reaction is produced because of its high electronegativity. Then the important feature to study is what happens in the aromatic ring when it changes to the tetraolefin.

The accepted mechanism was shown in *Figure 1*, and is general for all kinds of substituted cyclophanes, and polymerization occurs by a concatenation mechanism for each unit of *p*-quinodimethane as shown in *Figure 4a*. During this process the molecule must take a polar form in order to join two entities and then continue in propagation. Finally, it would take the shape shown in *Figure 4b*.

This procedure requires the orientation of one electronic pair to give a negative charge in one side and a positive one in the other. This situation occurs with a weakening of the electron density of the ring, and this facilitates electron flow in the molecule. From this we can conclude that the withdrawing group will be the best target for successful polarization.

The chloride compound demonstrates a good yield of polymer in spite of its nature as an electron-releasing agent. The explanation of this effect comes from the ambiguity of this radical as a deactivator due to its high electronegativity. Its Δq_π is -309.6×10^{-3}, indicating a moderately high electron abundance. Therefore, we can expect that the polymerization reaction would require a large amount of energy, and this is the case since this process needs very high temperatures to obtain a good yield.

The cyano compound is a different case. The CN group has a Δq_π of 93.7×10^{-3}, indicating a low electron abundance. Then the π electrons of the double bonds in the *p*-quinodimethane compound can move more easily than in the other cases. There must be a macroscopic effect for this phenomenon, and certainly the cyano polymer is obtainable with good yields at low temperatures.

It appears that the key to obtaining polymers at low temperatures is related to the presence of an electron-withdrawing group. Here we have carried out our analysis on known compounds that can readily undergo the polymerization process, but it should be possible to obtain better yields using monomers with stronger electron-withdrawing groups (NO_2, CHO, CO_2CH_3, etc.). This proposition must be confirmed with experimental work.

CONCLUSIONS

The polymerization reaction of cyclophane and substituted cyclophanes follows a known mechanism that is reviewed in this paper. The intermediate molecule *p*-quinodimethane is very important in starting the polymerization process. It can result in two forms, a tetraolefin and an aromatic biradical. The energy difference between these is obtainable in the environment of reaction, but there is little evidence favouring the free-radical pathway. The above results were obtained from theoretical calculations, and good agreement is found with the respective experimental results.

The main feature ruling the reaction conditions seems to be the nature of the substituent on the aromatic ring. In this sense we have carried out a theoretical analysis based on the Taft and Topson rules for aromatic compounds in order to model a suitable process. The best target for an easy polymerization process is a cyclophane substituted with an electron-withdrawing radical. In this work CN substitution was analysed. It has been demonstrated that it presents the possibility of a lower-temperature polymerization than is the case for the chloride-substituted ring. Further work will include the development of experimental work on cyclophane derivatives containing electron-withdrawing groups.

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