Thermally Promoted Elimination and Substitution Reactions in Poly(*p*-arylene vinylene) Precursor Polyelectrolytes

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ABSTRACT: The thermal conversion of dialkylsulfonium polyelectrolyte precursor polymers **1b**−**e** to poly(*p*-arylene vinylene)s was studied by direct pyrolysis mass spectrometry in order to elucidate the mechanism of the sulfonium elimination reaction. The temperature dependence of the single ion currents of the four more abundant volatile products was correlated with the structural changes introduced in the arylene moiety of the polyelectrolytes and with the counterion nature. Experimental results suggest that the elimination reactions in the solid state proceed through an E2 mechanism.

Introduction

Poly(arylene vinylene) polymers of general formula $[-Ar-CH=CH-]_n$ are one of the most promising class of conjugated polymers that are currently under investigation, both from the viewpoint of understanding fundamental electronic processes and for practical applications in optoelectronics.[1] In addition to possessing a delocalized electronic structure, the poly(arylene vinylene)s have the advantage of being prepared via a synthetic route that allows considerable flexibility for sample preparation. This polymerization procedure involves first the synthesis of a soluble precursor polymer **1a**. The intermediate polyelectrolyte can then be cast into films of any dimension by solvent evaporation or spin-coating techniques. A simple heat treatment of these films affords fully dense homogeneous thin films of poly(phenylene vinylene), **2**, PPV.[2] Though processability can also be achieved by attachment of lateral chains to improve polymer solubility, none of the numerous polymers synthesized by this alternative route[3] have the thermal stability or photostability of the unsubstituted PPV obtained by the sulfonium salt route.[4]

However, side reactions will produce defects in the polymer backbone and will have deleterious effects on the conjugated polymer optoelectronic properties. So, significant efforts have been made to understand the thermal elimination process and to evaluate the side reactions that introduce saturated units or conformational defects that interrupt the polymer conjugation.[5−12] Nevertheless, the mechanistic nature of the main elimination reaction is still not fully unraveled. While early reports[2,7] assigned an E1cB mechanism without much experimental support, later studies seem to favor either an E2 process[8] or an E1 process.[13,14]

We report here on how structural variations in the polyelectrolyte aryl moiety affect the thermal elimination reaction and its side reactions. We studied the thermal processes that occur within the polymer film by direct pyrolysis mass spectrometry (DPMS) of the polyelectrolytes **1b**−**e** (see Scheme 2).

We tried to fit all the observed data into a general reactivity pattern. By assessing the extent in which the

Scheme 1
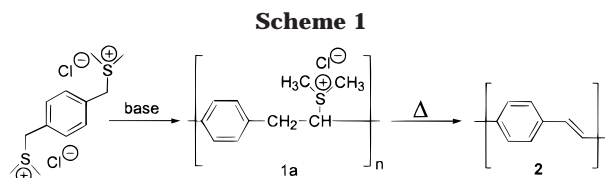
structural changes facilitated the elimination reactions, we also tried to confirm the assignment of an E1 mechanism as well as to analyze whether this mechanism is operative in different PPV precursor polymers. This standard mechanistic approach has been extensively used by us[15] and many others[16] for base-promoted elimination reactions performed in solution and in the gas phase. In addition, molecular modeling of the polyelectrolyte repeating units was done to help with data interpretation.

Experimental Section

The monomers and their corresponding polyelectrolytes **1b**, **1c**, **1d**, and **1e** were synthesized and purified according to reported procedures.[7,17] The thermal reactions were performed using a custom TGA/mass spectrometer (Cahn microbalance/Granville Research Finnigan 200 quadrupole mass spectrometer). These data were obtained by Systems Research Laboratories, Dayton, OH. Samples (ca. 5.0 mg) of each polyelectrolyte were heated at a scan rate of 3 K min^{-1} under a initial vacuum of about 10^{-7} Torr. The total ion current (TIC) and the single ion currents (SIC) were recorded at intervals in the 50−950 °C temperature range. However, here we report only the SIC data recorded for the four more abundant products generated in the pyrolysis up to 400 °C since all the relevant processes for this study occurred below this temperature. Molecular modeling was performed using PM3 program as implemented in Hyperchem.[18]

Results and Discussion

The combined thermogravimetry−mass spectroscopy (TG-MS) for polymers **1b**−**d** showed that the weight loss is correlated with the increase in the TIC, but both broad maxima occurring at 90 and 400 °C give only limited information about the complexity of the reactions that are taking place within the polymer film. Much more informative are the SIC traces depicted in Figure 1.

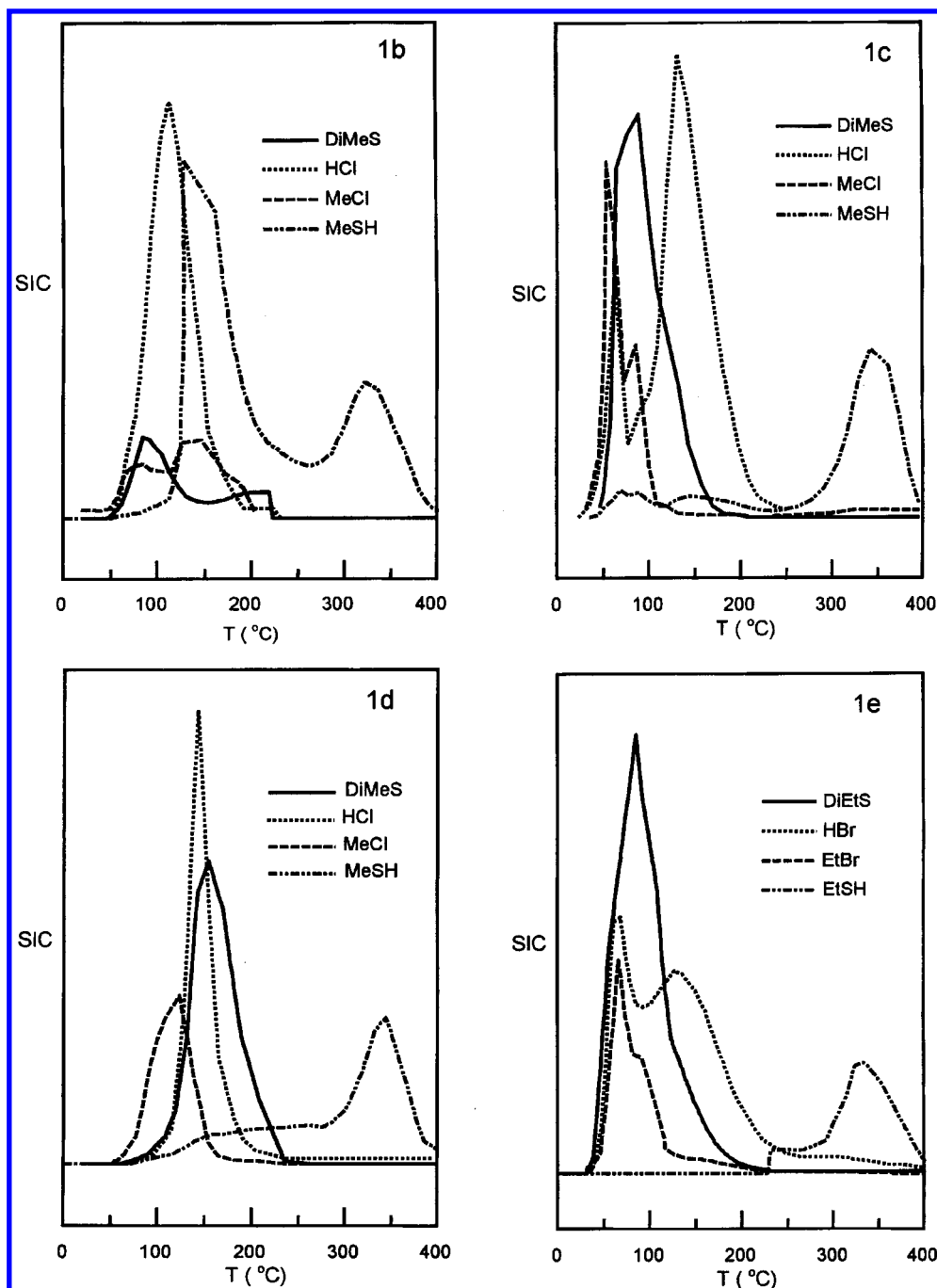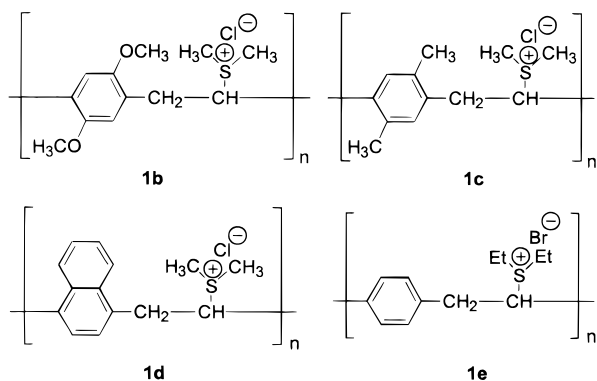* Corresponding author. E-mail rgaray@criba.edu.ar.

Figure 1. Single ion current (SIC) traces of the four more abundant products (excluding water) generated in the pyrolysis of polymers **1b**–**e**.

The DPMS results must be analyzed within the framework of the most probable reaction sequence. Scheme 3 shows the substitution and elimination reactions that are possible on a repeating unit of the unsubstituted polymer **1a**.
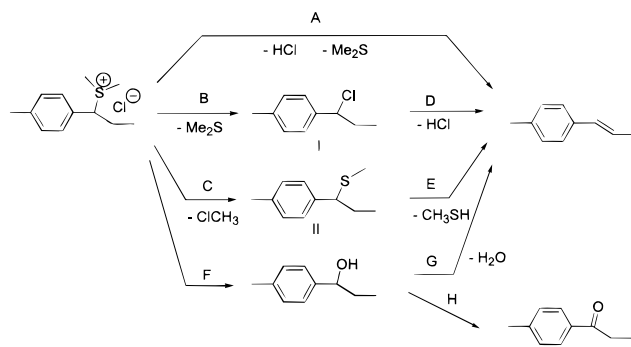
First, the reaction sequences that led to the conjugated polymer have two concomitant fundamental mechanistic pathways; namely, the desired elimination reaction A and a few unwanted substitution reactions. At least this basic mechanistic fact seems now to be well established for the unsubstituted phenyl (R = H) polyelectrolyte **1a** despite some suggestions affirming that the incidence of the substitution reaction by chlorine on the backbone saturated carbon (pathway B) is irrelevant.[14] Thus, the analysis by DP-IR and DP-MS of the HCl evolved showed two maxima at ca. 100

and 180 °C that can be interpreted as being originated from pathways A and B, respectively. On the other hand, the occurrence of the substitution on the sulfide saturated carbon (pathway C) has also been demonstrated since the change from dimethyl sulfide to cyclic sulfides was proved to be beneficial in reducing the number of polymer backbone defects.[6] In fact, in this work we used the dimethylsulfonium derivatives instead of the cyclic sulfide type because the relative incidence and timing of the competing substitution reactions are better assessed by using the former derivatives. Moreover, the retention of chlorine in the polymer structure due to the substitution reaction C (see Scheme 4) will obscure, in the case of the cyclic derivatives, the analysis of the evolved gases and its mechanistic implications.
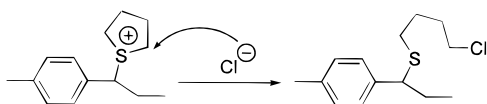
Scheme 2

1b   **1c**

1d   **1e**

Scheme 3

Scheme 4

Table 1. SIC Maxima of Volatile Products Generated in the Thermal Elimination of Polyelectrolytes 1b−d[a]

polyelectrolyte	Me$_2$S	HCl[b]	MeCl	MeSH
1a[c]	120	80	85	360
1b	90	115	80[d]	340
1c	80	60	55	340
1d	155	150	120	334

[a] Of the four more abundant compounds excluding water, in °C. [b] Only the first maximum is reported. [c] Data taken from ref 6. [d] A second maximum at 142 °C was observed.

absence of DMS. Finally, the detection of MeSH will indicate that reaction E is taking place.

It should also be kept in mind that the amount of the evolved gases is only proportional to the SIC peak observed. Then, the relative intensity of the SIC peaks provides only semiquantitative information since the unknown ionization efficiencies are different for each ion.

Our results shown in Figure 1 indicate that the reactivity pattern depicted in Scheme 3 is essentially common to all of the polyelectrolytes studied regardless of the structural variations on the aryl moiety. In that way, we observed that the evolution of entrapped and solvated water in the films that starts at ca. 50 °C in the four polyelectrolytes is concurrent with a series of reactions on the polyelectrolyte. All these elimination and substitution processes occur at temperatures below 200 °C with the exception of MeSH elimination, which occurs mainly at ca. 340 °C. The SIC data for polymers **1b−d** are summarized in Table 1 along with the results reported previously for the unsubstituted polyelectrolyte **1a**.[2]

In all the studied polyelectrolytes the first reaction to be initiated is the substitution on the methyl carbon (reaction C). In particular, for polyelectrolytes **1b** and **1c** this substitution reaction is promptly followed by the elimination A. On the contrary, for the polyelectrolyte **1d** it is the only significant reaction at temperatures below 100 °C since the elimination reaction A occurs at higher temperatures. The apparent lower sensitivity of reaction C to structural variations can be ascribed to the exposed position of the methyl carbon to nucleophilic attack which will be little influenced by structural changes at the polymer backbone. The occurrence of a second CH$_3$Cl peak in the polyelectrolyte **1b** at higher temperatures will be elaborated later.

A significant second HCl peak at 135 °C in the case of **1c** and a displacement of the HCl peak with respect to the DiMeS peak for **1b** suggests that the substitution reaction B is a common process for **1a**, **1b**, and **1c**. The product thus formed is eliminated then at ca. 150 °C. However, it is not possible to know whether this reaction is taken place in **1d** since the products from the elimination A evolved in this temperature range.

It has been frequently observed that the evolved HCl has a beneficial effect in perfecting the conjugated character of all polymers since it promotes the elimination of some of the sulfide and hydroxylic defects.[13] The acid-promoted CH$_3$SH elimination can be inferred from the evolution of CH$_3$SH from the polymers **1b−d** at ca. 150 °C, which can be considered as occurring in these cases at rather low temperatures when the poor nucleofugal ability of the methyl sulfide group is taken into account. In fact, in Table 1 it can be seen that for all four polymers this process takes place in the absence of HCl at ca. 340 °C. Moreover, several reports have stressed the ability of HCl to promote MeOH and MeSH

Second, there are a series of elimination reactions on the substitution products moieties I and II (see Scheme 3) that contribute to extend the conjugation in the polymer backbone and therefore to improve the polymer properties (pathways D and E). Finally, it has not to be overlooked that the nucleophilic attack of the water present in the film (pathways F) will lead to HO− defects that, in turn, can be eliminated or originate carbonyl defects (pathways G and H).[12,19] The contribution of the solvolitic reaction to generate backbone defects is particularly important in polymer **1b**;[1c] however, since this reaction occurs mainly in solution and is not related to the elimination reaction, it will not be further discussed. Though this overall scheme seems to be rather complex and not completely understood yet, the empirical and careful search for optimal polymerization and thermal treatment conditions has led to materials with excellent properties.

In principle, several considerations have to be done in order to analyze the gas evolution due to the four most abundant products of the thermal treatment and to relate them to reasonable reaction pathways. To begin with, we consider that the concurrent evolution of both DMS and HCl indicates that the desired elimination A is taking place in that temperature range while the detection of CH$_3$Cl makes evident the concomitant substitution reaction at the methyl carbon. Therefore, it follows that the method cannot provide information about the other substitution reaction B which is promoted by the chloride ion since the product, DMS, will be masked by the DMS originated by the elimination A. However, the occurrence of this reaction will be brought to light by posterior evolution of HCl in the

elimination. This fact also suggests that the second CH₃Cl peak which is observed only for **1b** indicates that some of the MeOAr groups on the aryl moiety have been cleaved by the HCl evolved. Undoubtedly, the acidity of HCl and the nucleophilicity of the chloride ion, either being unsolvated or poorly solvated, will be much increased in these media.

The nonionic reaction that takes place above 200 °C, i.e., the uncatalyzed elimination of MeSH at 340 °C, is a radical process which shows a remarkable insensitivity to electronic or steric effects. These results agree with the general conclusion that all homolytic eliminations are two-step processes.[20] Indeed, the C−S bond strength is probably the only factor of importance that sets the temperature threshold for this reaction since its cleavage will provide the radicals needed to abstract the β hydrogens in the benzylic positions of the polymer backbone and to initiate a chain reaction. We also observed weak SIC signals corresponding to MeSSMe, MeSSSMe, and H₂, but these results are not presented here since they originate from the gas-phase reactions of MeSH and bear no significance for the present analysis.

Different mechanisms have been discussed and assigned to reaction A. While the E1cB stepwise process can be safely discarded on the basis of structural considerations since no strong base is present, an electron-withdrawing group capable of stabilizing the β-carbanion is lacking, and the sulfonium group is one of the best leaving groups, the assignation of an E1 mechanism instead of an E2 apparently rests solely upon the observation of a DMS peak at 125 °C coupled with the occurrence of a HCl peak at 195 °C.[13,14] In our view, however, the evolution of HCl gases at 160−200 °C should be considered only as an indication that an elimination of HCl is taking place. Hence, we consider the HCl evolution at ca. 160 °C as a indication that reaction B is being followed by D, instead of interpreting it as evidence that supports the assignation of a two-step mechanism of the E1 type to reaction B. In addition, it is unlikely that a carbocation could survive long as such, i.e., several minutes as the heating rate of the DPMS experiments would require, in the harsh conditions of the thermal treatment until the chloride ion abstracts a benzylic proton. Thus, no mechanistic evidence regarding the nature of the elimination reaction can be drawn from the appearance or the absence of this HCl peak.

We tried to assess instead the extent to which structural changes affected the elimination reaction. So, variations in the aryl moiety of the polyelectrolyte were made to gather thermodynamic data that could be used to elucidate the elimination reaction mechanism. In principle, the methoxy groups in **1b** as well as the naphthalene moiety in **1d** should stabilize the carbocation generated in a E1 process, causing in this way the elimination reaction to occur at temperatures lower than those reported for the parent polyelectrolyte. Smaller but similar effects can be expected from the methyl substitution in **1c**. We observed, however, that the temperature ranges in which elimination reactions proceeded did not follow this pattern. Thus, when compared with the parent polyelectrolyte, the introduction of methyl groups in the aryl moiety facilitates the elimination as much as the methoxy groups do. On the other hand, the extension of the π system in **1d** delays the onset of the elimination by ca. 60 °C, suggesting that
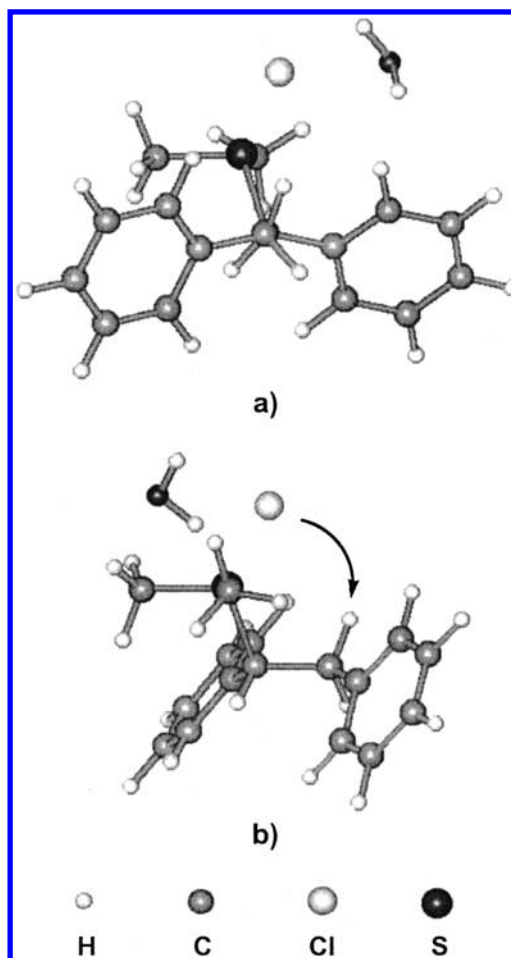

Figure 2. PM3 conformation of a polyelectrolyte **1a** repeating unit: (a) Newmann projection of the two benzylic carbons; (b) side view, the arrow points to the benzylic hydrogen which could be abstracted by the chloride ion.

steric effects are operative. In fact, a similar trend has been observed during the synthesis of poly(anthrylene vinylene)[21] and poly(phenylphenylene vinylene).[22] The TGA analysis of the polyelectrolyte precursor of these polymers showed that the maximum of the weight loss derivative occur at 170 and 180 °C, respectively. For polymer **1d**, if the E1 mechanism were operating, the naphthalene group should stabilize the carbocation while the interaction between the hydrogen in 8-carbon of the ring and the hydrogen atoms on the α-carbon could be minimized by adopting an alternated conformation in the rate-determining step. So, stabilizing polar effects will be dominant since the destabilizing steric ones could be minimized. On the contrary, the destabilizing steric interaction cannot be avoided due to the planarization of both carbon atoms in the case of the E2 mechanism. In summary, this pattern is consistent with a concerted reaction of the E2 type in which the stability of the incipient olefinic bond plays an important role in determining the transition-state energy.

Moreover, a marked dependence of the elimination temperature on the counterion nature has been observed previously.[5,11] In agreement with these studies, our results shown in Figure 1 indicate that the elimination in the sulfonium bromide polyelectrolyte **1e** takes place at lower temperatures than the sulfonium chloride polyelectrolyte **1a**. Though it is difficult to assess the water content in all these films at the moment of the

DPMS analysis, our and others[6] elemental analysis data indicate that an average of one-half to two molecules of water per polyelectrolyte repeating unit can be present near the sulfonium chloride group in free-standing films cast from water and stored for several weeks. Even though variable and dependent on handing and storage conditions, the amount of water is rather limited even at the beginning of the thermal treatment. The poorly solvated halide ion can be considered then as being in a situation more akin to that of the naked ions and able to act as a strong base. Therefore, the dependence of reaction on the counterion nature points then to a strong involvement of it in the elimination process as it will be in the case of an E2 process. Nevertheless, it is difficult to rationalize the fact that the bromide ion, being a weaker base, starts the elimination reaction at lower temperatures than the chloride ion in a trend opposite to the one observed with poorly solvated ions. In this context, it is expected that the chloride ion, which is a harder base than the bromide ion according to Pearson's HSAB principle, should behave as a better base than the softer bromide ion when it attacks the hard proton and should thus facilitate the E2 elimination.

All previous studies, as well as our data, coincide that the carbon−carbon double bonds originated from these thermal eliminations have a trans configuration. To illustrate how the trans olefinic configurations could be originated, we performed the molecular modeling of the polyelectrolyte **1a** repeating unit conformations, as well as of all other polymers **1b**−**e**, at the PM3 semiempirical level. Of the three possible alternated conformations of polyelectrolyte **1a** repeating unit, the one that has the bulky phenyl groups in an anti arrangement is depicted in Figure 2a. As can also be observed in Figure 2b, the calculations suggest that the halide ion could be in a prime position to promote a syn elimination by abstraction of a benzylic β-hydrogen to render the trans carbon−carbon double bond. This alternative stereochemical route to the anti elimination has been demonstrated to be operative when electrostatic interactions between the attacking base and the leaving group exist in the reacting system as it is in the present case.[23,24] The modeling was performed without and with the inclusion of water molecules in order to mimic the average solvation of the sulfonium chloride group as the elemental analysis results indicated. However, no significant conformational or geometrical differences between the solvated groups with one and two water molecules and the unsolvated groups were found.

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