Electrical, Thermal, and Photo Properties of Poly(phenylene vinylene) Precursors. II. Microwave-Induced Elimination Reactions in Precursor Polymer Films

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SYNOPSIS

Microwave radiation (MWR) was used to induce the elimination reaction of the poly(phenylene vinylene)–polyelectrolyte precursor polymer (PPV precursor) into the fully conjugated polymer. The process was applied mainly to the unsubstituted PPV and was followed by infrared spectroscopy. The extent of the elimination process was also determined from the amount of residual sulfur in the film after the irradiation process. The microwave-induced elimination process was also attempted using PPV precursor films that had been impregnated with anionic compounds containing iron. The molecular mechanisms for the observations are discussed and comparison with the elimination reaction induced by other energy sources is also made. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Although almost 16 years have already passed since the observation by Shirakawa et al. that polyacetylene could be doped by I_2 molecules and have its electrical conductivity greatly increased,[1] the field of conducting polymers keeps growing with new applications continually appearing. This development is particularly true for the areas of optics[2] and electronics,[3] although various other fields have been affected including such diverse branches of chemistry as electrochemistry[4] and catalysis.[†]

Because there appears to be a direct relationship between the unidirectionality of the molecular conducting pathway and an increase in interchain interactions, these polymers cannot be easily dissolved or melted. This behavior poses a great challenge to the processing of these materials, but there are some ways to decrease interchain interactions. One of the most commonly used methods is to add a flexible

side group to the main chain. This type of substitution causes a considerable decrease in the melting point and has been extensively used in the development of liquid crystal polymers.[5] Most recently, the same strategy was utilized by Wudl and coworkers[6] and by Garay and Lenz[7] for the development of soluble PPV derivatives.

Another way to bypass the problem of processability of the conducting polymers is to synthesize them through a soluble or fusible precursor polymer. This procedure has been used to prepare polyacetylene,[8] polyphenylene,[9] and the poly(phenylene vinylene) (PPV) family of polymers.[10] The basic principle is to prepare first a polymer that can be dissolved (in water or some organic compound) or easily processed by standard physical procedures. After obtaining a film of the precursor polymer, by casting or melt processing, the precursor polymer is converted to the fully conjugated polymer by a thermal elimination step. Figure 1 shows the reactions involved in the synthesis of the sulfonium salt, polyelectrolyte precursor polymer for PPV.[11,12] The polymerization of the bis-sulfonium salt is carried out under basic conditions in the absence of oxygen to form the high molecular weight, sulfonium polyelectrolyte.[10,13] The final step in the conversion of the polyelectrolyte to PPV is an elimination reaction, in which the organic sulfide and hydrogen ha-

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lide are released, and the fully conjugated chain is formed.

It is of interest to note that the last step in the reaction sequence in Figure 1 involves an energy-exchange process between an energy source and the polyelectrolyte precursor film. Normally, a thermal energy source is used for this purpose, but, of course, other types of energy sources could also be used. Recently, the absorption spectra of some PPV derivatives have been modified by attaching anionic azosulfonic dyes to the positive sites of the polyelectrolyte precursor, and this modification allowed the use of a laser-induced elimination process.[14] Other energy sources, such as an electron beam, have also been used for that purpose.[15] If other efficient processes are to be found, the main requirement is a strong interaction cross section between the source and the polymer film.

The microwave region (MWR) is the region of the electromagnetic (EM) spectrum with frequencies from 100 MHz to 300 GHz. Molecules in the gas phase may interact with the MWR by resonant excitation to high-energy rotational levels. However,
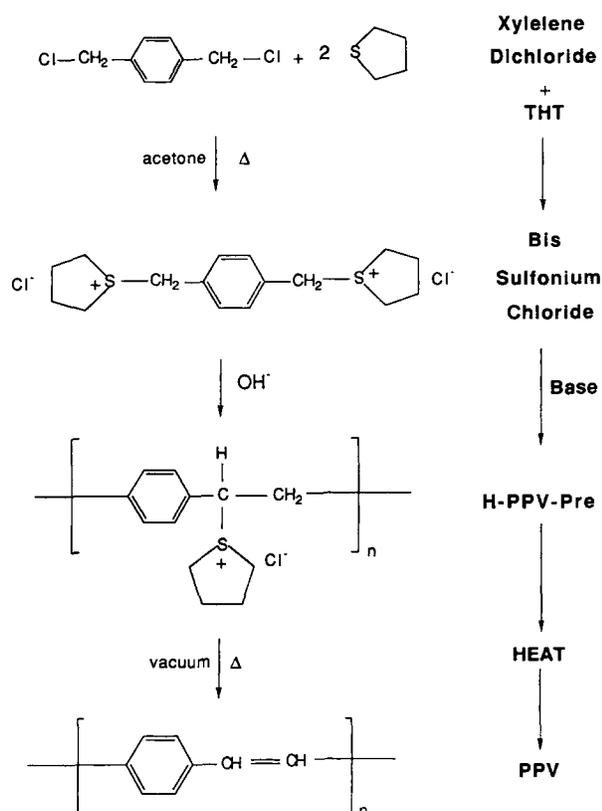

Figure 1   Reaction steps in the sulfonium polyelectrolyte precursor route for the preparation of PPV-type polymers.

when in the liquid or in the solid phases, the interaction occurs mostly by a nonresonant process. In these cases, the main coupling mechanism between MWR and the material involves the charge distribution inside the molecular structure, and this interaction is determined by the dipole moment and, consequently, by the complex permittivity, K^*, of the material.[16] This property is mathematically represented by the following equation:

$$K^* = K' - jK'' = |K|e^{-jd} \qquad (1)$$

where K' is the dielectric constant and K'' is the dielectric loss or loss factor of the material. The dielectric constant is a measure of the material's ability to store electrical energy, whereas the loss factor is related to the ability of the material to dissipate electrical energy. These properties may also be expressed by a quantity called loss tangent, $\tan d$, such that

$$\tan d = K''/K' \qquad (2)$$

and its value expresses the material's ability to be penetrated by an electrical field and to dissipate electrical energy as heat.

Depending on the materials dielectric characteristics, microwaves (MWs) can be used for various modes of heating and excitation processes. Recently, many different applications of microwaves to chemical processes have appeared in the literature. These include the use of MW dielectric loss heating for accelerating the rates of organic reactions,[17] the syntheses of organomettalic[18] and coordination compounds,[19] solid-state reactions,[20] and drying of different types of materials.[21] MWs have also been used to initiate polymerization reactions,[22] for cross-linking polymers,[23] and for curing composites.[24] With respect to the polymerization-induced reactions, the processes related to the use of polymers in dental applications have received the greatest attention,[25] although the interaction of MWs with foods is probably the most thoroughly studied of all areas.[26]

As clearly seen in eq. (2), there is an inverse relationship between the ability of the material to absorb and dissipate the nonresonant MWR and its dielectric constant. The presence of water inside a material, with a dielectric constant of about 80 at room temperature, is a first condition for strong coupling with an MW field and this is the interaction basis for cooking foods.[27]

The work that will be described in this report is based on the observation that the elimination pro-

cess in a precursor film is greatly increased in rate upon drying, after casting the film from an aqueous solution. The water inside the film, because of its high dielectric constant, offers the possibility of an efficient coupling of energy transfer from an MW source. This report, therefore, is concerned with the use of such an electromagnetic source to induce the elimination process of some PPV precursor films into the conjugated PPV form.

EXPERIMENTAL

The precursor polymers of both the substituted 2,5-dimethoxy derivative, DMEO–PPV, and the unsubstituted poly(phenylene vinylene), H–PPV–Pre, were prepared by the bis-sulfonium salt precursor route[12] with some of the modifications introduced by many laboratories over the years.[10,28–30] In the procedure adopted in this study, the sequence of synthetic steps were the following: (a) Chloromethylation of the appropriate benzene derivative[16] (if the dichloride is not commercially available). (b) Reaction of the xylelene dichloride with tetrahydrothiophene (THT)[29] to form the bis-sulfonium salt. (c) Polymerization of the bis-tetrahydrothiophenium salt to form the cationic, polyelectrolyte precursor. The last step was conducted under Ar flow and under basic (NaOH) conditions. The reaction medium consisted of a mixture of water and pentane in a volumetric ratio of 1 : 2.[30] (d) In some cases, the solution of the polyelectrolyte precursor was dialyzed for at least 4 days to eliminate the sodium and chloride ions present and to obtain polymers with a weight-average molecular weight, M_w, greater than 6000. (e) Films were cast by water evaporation. In the case of the DMEO–PPV precursor, films could also be obtained by filtering the solution containing gel particles using a Buchner filter with a sintered glass bed having a pore diameter of 20 μm or less, then drying the gel.[31] This process was much faster and spent much less energy than the vacuum evaporation procedure. The films thus formed were cut to rectangular pieces (25 $\times$ 30 mm) and glued to a microscope glass slide containing a central slot. This arrangement allowed direct spectroscopic observation before and after the MW treatment.

The assembly (film plus support) was placed in a glass vessel and the system was evacuated to a pressure range between 10^{-3} and about 10^{-2} Torr. The sample system was placed on top of the rotating plate of an MW oven, to expose it to a more homogeneous average field, and irradiated. The MW oven used, a Model MDS 81D from the CEM Co., operated at an average power of 600 W. After different irradiation periods, the sample was submitted to spectroscopic observations and/or to elemental analysis.

The IR spectra were recorded using a Perkin-Elmer Model 1320 dispersive spectrometer. A Cary spectrophotometer (Model 2300, from Varian) was utilized for observations in the visible and ultraviolet (VIS-UV) regions of the electromagnetic spectrum. Elemental analysis were performed at the University of Massachusetts Microanalytical Laboratory.

RESULTS AND DISCUSSION

In two separate experiments, the direct interaction of MWR with H–PPV–Pre was observed by placing two samples inside the oven, one supported on a Teflon plate and the other on a glass plate. The irradiation treatments last 3 h and both were performed in open air. The extent of elimination was determined by two different procedures. First, the IR spectra of the samples were recorded before and after the irradiation procedure. The results of this study are shown in Figure 2, in which (a) is the spectrum of the precursor film before the irradiation, (b) is the spectrum of the sample placed on the Teflon support, (c) corresponds to the sample placed on the glass plate, and (d) is the spectrum of a fully eliminated H–PPV film ($T \sim 240°C$ for 24 h).

It is clear that some water loss occurred by this treatment as indicated by the decrease in intensity of the absorption band near 3350 cm^{-1}. It is also apparent from the IR spectra that the glass-supported sample had less water than did the Teflon-supported sample as indicated by the relative intensity of the water peak at 3350 cm^{-1} compared to the aromatic and aliphatic C — H stretching vibrations in the 3000–2800 cm^{-1} region. However, although water loss can accelerate the elimination reaction, the difference observed is not significant, and a quantitative relationship for the degree of elimination of each sample could not be immediately established from the IR spectra.

A better evaluation of the extent of elimination was possible by determining the amount of residual sulfur in the samples after the MW irradiation. These results are shown in Table I, in which the amount of sulfur for the glass-supported sample (S_g) is presented along with the sulfur content of the Teflon-supported sample (S_t) and the percentage of sulfur present in the original sample (S_o). It is clear from these results that both samples had undergone
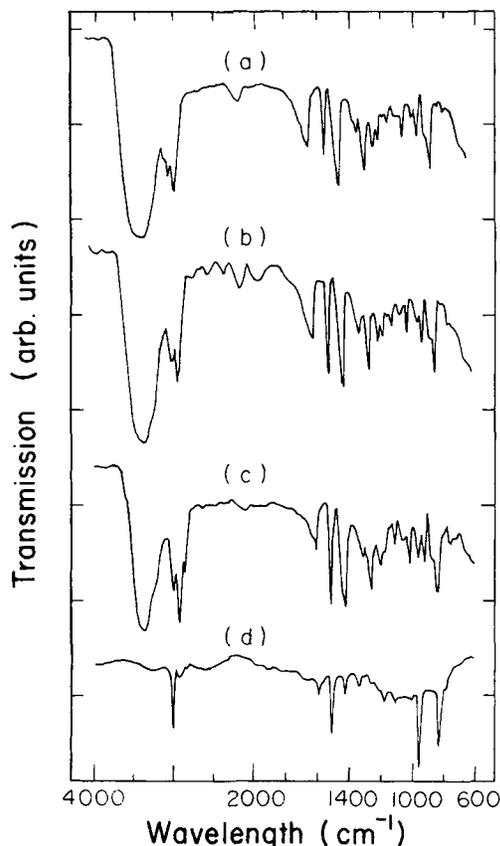
Figure 2 IR spectra of H-PPV-Pre polyelectrolyte precursor films (a) before irradiation; irradiated for 3 h in open air and supported either by (b) a Teflon plate or (c) by a glass plate; and (d) a thermally eliminated ($T \sim 220°C$) H-PPV sample.
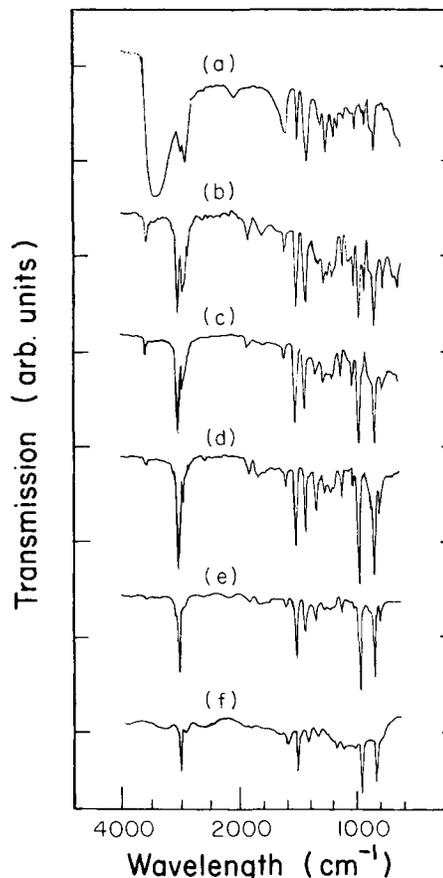

Figure 3 IR spectra of H-PPV-Pre polyelectrolyte precursor films (a) before irradiation and irradiated under vacuum inside a glass container for (b) 0.5, (c) 1.0, (d) 2.0, and (e) 3.0 h; also included is the spectrum of a thermally eliminated H-PPV sample (f).

some elimination and that the Teflon-supported sample became slightly more conjugated than did the other.

After these initial results, a different irradiation procedure was performed using an evacuated glass vessel, as described in the Experimental section. H-PPV-Pre films obtained by the same casting procedure were irradiated for different periods of time. Their IR spectra were recorded before and after the MW irradiation. Figure 3 shows the spectra of these

Table I Sulfur Content (%) of H-PPV-Pre Samples Before (S_o) and After 3 Hours of MW Irradiation at Ambient Conditions

	S_o	S_g[a]	S_t[b]
Sulfur	10.02	9.41	9.14

[a] S_g, sample on a glass support.
[b] S_t, sample on a Teflon support.

films before irradiation (a) and after the following irradiation times: 0.5 h (b), 1.0 h (c), 2.0 h (d), and 3.0 h (e). Also included in Figure 3 is the spectrum of a fully eliminated H-PPV film (f).

To better explain the changes in the IR absorption spectra of the MW-irradiated samples, it is necessary to consider the chemical reactions that occur during the elimination process (Fig. 4). First, the number of CH_2 groups decrease and vinylene groups are formed instead, as evidenced in Figure 3 both by the decrease in intensity of the symmetric and asymmetric C — H stretching vibration bands between 2800 and 3000 cm^{-1} and the simultaneous appearance of the C — H stretching vibration band of the *trans*-vinylene group (the very sharp band near 3000 cm^{-1}). At the same time, the band at 1420 cm^{-1} became sharper because of the decrease in intensity of the bending mode band of CH_2, which is seen as a shoulder in the spectrum of the nonirra-
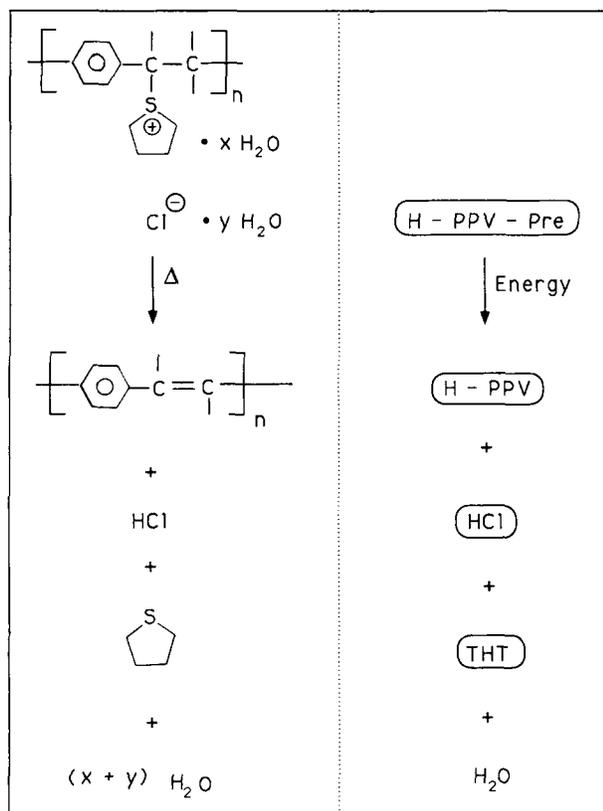
Figure 4   Schematic representation of the elimination reaction of precursor films to form the fully conjugated H-PPV chain.

Figure 5   Intensity of a THT band near 1194 cm^{-1} plotted against the amount of residual sulfur in the MW-irradiated films.

diated sample [Fig. 3(a)]. The CH$_2$ groups in the polymer are not the only groups of this type that will decrease in amount (forming vinylene bonds), but also the CH$_2$ from the tetrahydrothiophenenium group (scissor mode) will change. Other bands that probably belong to the tetrahydrothiophene species are the absorptions at about 1310 cm^{-1} (CH$_2$ wag), 1260 cm^{-1} (CH$_2$ wag), 1200 and 1018 cm^{-1} (THT ring vibrations), a strong shoulder around 880 cm^{-1} (CH$_2$ rock), and a C—S—C vibration at about 670 cm^{-1}.[32] These bands steadily decreased in intensity while new ones appeared and some of the old bands changed slightly in their shape, because of the overlap with bands belonging to disappearing groups.

The bands corresponding to fully eliminated H-PPV shown in Figure 3(e) and (f) have been assigned before.[33] A few attempts were made to correlate the intensity of the peaks that appeared or disappeared with the amount of residual sulfur and the MW irradiation time. These correlations are shown in Figures 5 and 6, in which the intensity of the band near 1194 cm^{-1}, assigned to a THT ring
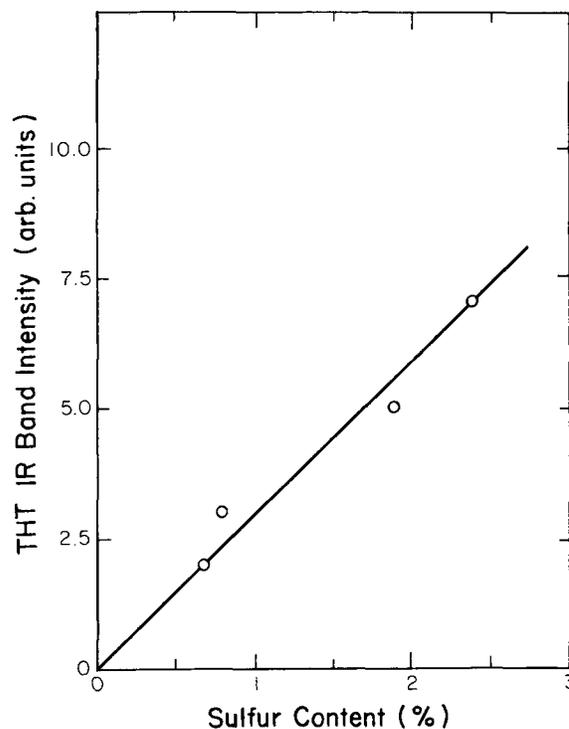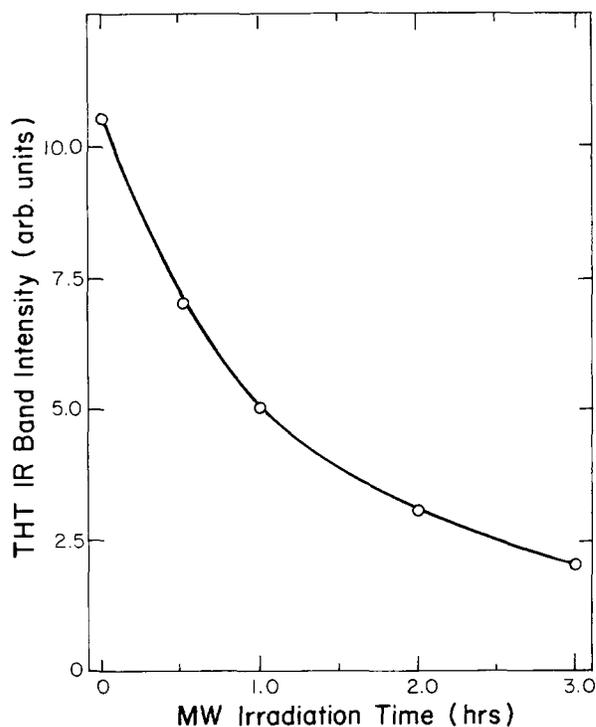
Figure 6   Intensity of a THT band near 1194 cm^{-1} plotted against the MW irradiation period.

vibration, is plotted against the amount of sulfur in Figure 5 and against the irradiation time in Figure 6. The experimental data represented in Figure 5 falls on a line passing through the origin, which is reassuring for the assignment of the 1200 cm^{-1} absorption peak to a THT ring vibration. However, because of the overlap of adjoining bands, and the consequent difficulty in measuring the band intensity, this linear correlation observed has to be taken as only a semiquantitative relationship between the variables.

Although the use of the IR spectra seems to be a good method to correlate the extent of the elimination reaction with the irradiation time, a more quantitative relationship can be established by measuring the amount of residual sulfur present in the films after the irradiation period. This correlation is shown in the plot of Figure 7. The data used are also represented in Table II, and these data correlate quite well in a linear fashion, except for the last point, which corresponds to the 3 h irradiation time. The amount of sulfur remaining in the film after 2 and 3 h of irradiation was basically the same as the residual sulfur present in the H–PPV films that were thermally eliminated between 220 and 300°C for 20–30 h periods.
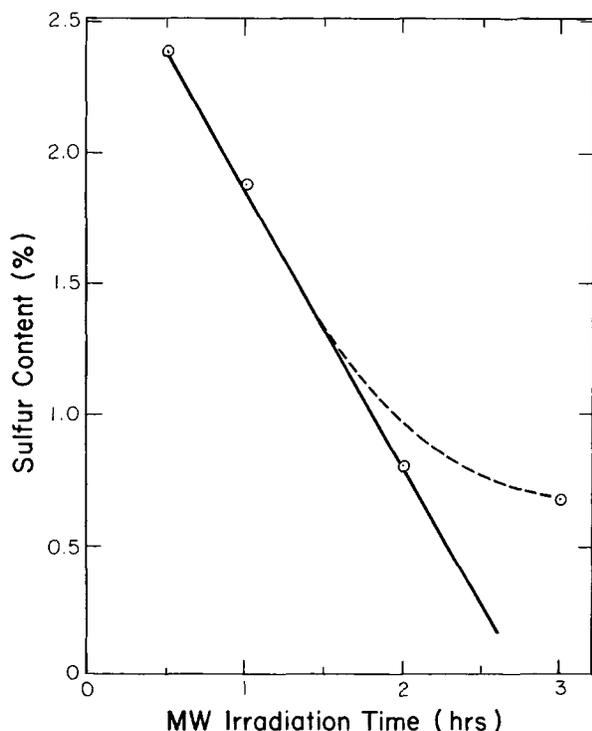
Table II Sulfur Content (%) of H–PPV–Pre Films Before (t = 0.0) and After the Indicated Times (in Hours) of MW Irradiation

Irradiation Time	Sulfur Content
t = 0.0	10.02
t = 0.5	2.39
t = 1.0	1.88
t = 2.0	0.80
t = 3.0	0.67

It is worth noting that when one of the parameters related to the extent of elimination (e.g., either the intensity of the THT peak at 1200 cm^{-1} or the percentage of residual sulfur) was plotted against the irradiation time, the same trend was apparent; initially, there was a linear relationship between the two, but, at longer times, there was a clear deviation from linearity and a tendency for saturation. These two observations (Figs. 6 and 7) may be considered as evidence that the film elimination process proceeded through a sequence of elementary steps. First, a particular temperature had to be reached before elimination occurred, the vinylene group formed, and THT and HCl were released. These two products had to diffuse through the film to reach the surface and vaporize. Because of the small thickness of the film and the homogeneous distribution of water in the sample, the temperature should be fast equilibrated throughout the film. The evaporation of THT and HCl should not be difficult for the PPV–precursor molecules close to the surface and these will undergo elimination first. However, after further degree of elimination, THT and HCl molecules from deep inside the film will have to diffuse to the surface and this process requires more time. Therefore, the deviation from linearity in these two figures seems to indicate that the diffusion of THT and HCl through the film was the rate-determining steps in the overall elimination process.

Studies on the interaction of MWR and foods have generated a wealth of valuable detailed information relating not only the presence of water but also various other factors that have to be considered when MW-induced heating of a material is performed.[27,34] Among these factors is the consideration that, although the presence of water certainly helps increase the field-to-material interaction, this single condition does not guarantee an efficient heating effect and a consequent rise in the materials' temperature. Because most of the thermal energy is generated by molecular "friction," or thermal energy

Figure 7 Relationship between the amount of residual sulfur inside a H–PPV precursor film vs. the MW irradiation period.

dissipation induced by the alignment and relaxation of the water dipole moment in the presence of an alternating electric field, the heating efficiency would be greater if the water present was "loose"—in other words, not hydrogen bonded to other species or present as water of crystallization—and evenly distributed throughout the material. This is apparently not the case for the polyelectrolyte precursors films in which the water is expected to be tightly bond to both the tetrahydrothiophenium ions and the chloride ions in hydration layers. This type of bonding of water to the polymers is probably one of the factors responsible for inefficient elimination when a small piece of the film was left openly inside the MW cavity.

It has also been observed that the volume of the sample loaded in the cavity has influence on the heating process, although the mechanistic base for such effects are still not totally clear.[26] This effect is believed to be related to the impedance matching between the MW cavity and the sample being irradiated; so, the intrinsic impedance of the material is inversely related to the complex permittivity[16] by the following equation:

$$n^* = n_0 (1/K^*)^{1/2} \qquad (3)$$

where n_0 is the intrinsic impedance of air.

It has been observed that energy transfer from the cavity to the sample is more efficiently accomplished if the intrinsic impedance of the material matches the impedance of free space [$n_0 \sim 377$ ohms].[26] This entity n is one of the major factors determining transmission and reflection of energy at mismatched dielectric boundaries. Although the dielectric characteristic of the precursor polymers were not measured in this study, it is apparent that these parameters, which have a more carefully documented role in the heating process of other organic materials, are playing a role in the present experiments, i.e., the tests in open air were performed with a very small sample (~ 100 mg) while the vacuum tests were carried out in a much bulkier container, which would improve the coupling between the sample and the cavity.

During some of the MW irradiation experiments, a violet-bluish glow was observed in some regions inside the glass container. This observation corresponds to a phenomenon called glow discharge, and in this case, it occurred because of the dielectric breakdown of air inside the evacuated glass vessel when the sample was submitted to the intense oscillating electric field[35] inside the MW oven. The gas molecules were ionized and the discharge inten-

sity depended on the pressure and on the magnitude of the electric field, which in this case was fixed and related to the MW oven power. In most of the experiments, the glow discharge occurred intermittently and lasted for the first few minutes of irradiation. Relevant to our observations is the fact that, because this discharge excitation process may generate species (mainly excited N_2 molecules) with very high vibration and electronic energy ($T_{el} \sim 3500$–4000 K[‡]) it may also make a contribution to the elimination process, i.e., although the pressure was relatively low (10^{-2} Torr), there could have been some electronic and/or vibration-to-vibration and vibration-to-translation energy-transfer processes. The impact of translation or vibrationally excited species with the precursor films may, therefore, also contribute to the elimination process.

Even with a low probability of direct coupling between the MW field and the material, due mainly to the tight binding of the water molecules to the ionic sites of the polyelectrolyte, it is clear, from the results presented, that MW can be used, in a reasonably efficient way, to increase the temperature of the material and induce the elimination process. However, there is some evidence that indirect heating effects may also be contributing to the elimination, from the observation that the films appeared with a stronger H–PPV–yellow color in the border regions, closer to the glass support. Although glass is known to be transparent to MWs,[36] the commonly used borosilicate-type glass may have some direct interaction with the MWs, in part because of the presence of magnetic impurities in its composition, especially iron, besides the above-mentioned influence of the size of the container in the MW interaction.

The process that appears to occur in these experiments, from the observations that drying the film leads to fast elimination, can be described as follows: Water, because of its high dielectric constant, greatly reduces the attraction between the anionic counter ion and the positive sites on the polymer chain. As soon as water is eliminated, the dielectric constant in that localized region of the structure is decreased (by about two orders of magnitude) and, as a consequence, a much higher electric attraction force develops between the charged and/or polarized species. After water evaporation, the final steps of the elimination reaction take place. The two most probable mechanisms are the following: (a) The Cl^- counterion acts as an efficient nu-

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[‡] See Ref. 22, p. 234, for a discussion on the phenomenon of breakdown.

cleophile, displacing the sulfonium group and forming a C — Cl bond.[29] The chlorine atom is later thermally eliminated by a dehydrochlorination process. (b) The Cl⁻ ion directly attacks a H atom from the polymer and elimination occurs by formation of HCl and THT. It is known that the temperature and time required for full elimination of the PPV precursors depend on which sulfide was used for the synthesis of the sulfonium salt. This observation seems to favor the first mechanism because the high temperatures ($T \sim 240$–$300°C$) and the extended periods of time (20–48 h) normally necessary for the complete elimination reaction are indicative that a strong bond (C — Cl) is being broken, instead of the simple evaporation of HCl and THT as the second mechanism suggests.

In addition to the effect of the electric field on dielectric heating, it is also possible to have a similar heating effect caused by the magnetic field component of the MW and the magnetic susceptibility of the material (a magnetocaloric effect[§]). Although there are no magnetic components inside the precursor polymer film, it is possible to introduce some anions containing magnetic species, by diffusion through the film and counterion exchange with the chloride, similar to the process previously described in our studies with dyes.[14] For this reason, attempts were made in the present study to attach $[Fe(CN)_6]^{3-}$ anions to the thiophenium site of the precursor by immersing a film of H–PPV–Pre in a solution of $K_3[Fe(CN)_6]$ ($c \sim 0.1$–0.2 mg/mL) in a 1 : 1 mixture of water plus isopropanol for periods of 4–8 h. The use of a magnetic metal in the anionic form was tried because of the strong interaction of the anion with the positive sites of the polyelectrolyte. It was hoped that the MW irradiation time could be greatly decreased by the introduction of a new (magnetic) contribution to the heat generating loss effects inside the film.

After immersing the glass-supported H–PPV–Pre film in the salt solution, it was examined by IR spectroscopy. Figure 8 shows the IR spectrum of a H–PPV–Pre film before (a) and after (b) immersion in a ferricyanide solution. The presence of a cyanide-containing species inside the polymer film was clearly evidenced by the presence of two very strong bands between 2100 and 2000 cm⁻¹. However, the C≡N vibration bands corresponding to the ferricyanide anion were expected to appear at slightly higher wavelength.[38] The bands observed matched better the positions for the C≡N bond in a ferro-

cyanide [Fe(II)] ion. This result is unexpected because the Fe(II) ion is known to be oxidized to Fe(III) under the experimental conditions used, so it is not yet clear why this change was observed.

Another interesting observation was made following the immersion procedure in the $[Fe(CN)_6]^{3-}$ solution. To assure that the observed spectral features corresponded to cyano species inside the polyelectrolyte film, and not on its surface, after the first observation [Fig. 8(b)], the film was extensively washed with distilled water, wiped with tissue paper, and left to dry at room temperature for about 12 h. A new spectrum was then recorded, and it is shown in Figure 8(c). It still shows the C≡N bands, but a surprising inversion in the relative intensity of the bands in the spectrum is immediately apparent. Subsequently, the salt concentration was doubled (to 0.2 mg/mL), with the goal of increasing the amount of iron inside the film, and it was reimmersed in the solution for 4.5 h, after which a new spectrum was recorded. This spectrum is shown in Figure 8(d), in which the initially observed intensity inversion is still evident and has increased in magnitude.
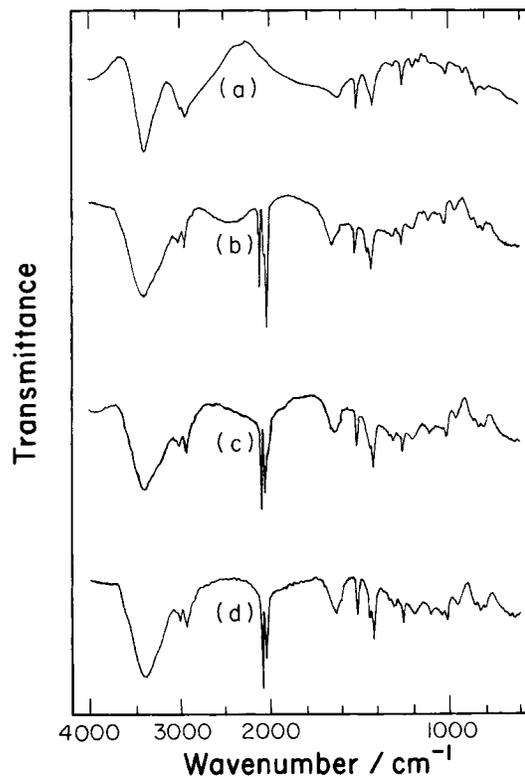

Figure 8   IR spectra of H–PPV–Pre films (a) before and (b) after immersion in a 1 : 1 water plus isopropanol solution of $K_3[Fe(CN)_6]$; spectra (c) and (d) correspond to time-dependent observations as described in the text.

[§] See, e.g., Ref. 37 for a theoretical discussion on the phenomenon.

The change observed is believed to result from inclusion of the ferricyanide ion at the cationic binding site of the thiophenium ion, with a possible change in conformation and symmetry with respect to the new environment and the consequent changes in transition probability intensities. However, it is not yet clear, at this moment, why, and how, this accommodation occurred and why these particular vibrational modes were directly affected by this dynamic effect. Further studies are necessary to better understand the details of the ion mobility inside the precursor film.

During the time of the MW irradiation experiment with a precursor film impregnated with the ferricyanide species, an intense glow discharge was observed, almost continuously, throughout the chamber. After the irradiation period, the sample was found to be totally destroyed, mostly carbonized. It is not clear why this happened during this particular irradiation process. Among the various possibilities, it may have been that, during this particular test, the vessel may have been pumped down to a pressure lower than in the previous experiments, thereby increasing the possibility of dielectric breakdown. The observation that the discharge lasted for the whole period of the experiment indicates that the glass container had no large leaks and held well under the pressure conditions. A second reason for the observation of a continuous and intense discharge could have been the increase of the magnetic contribution of the field interaction due to the presence of a magnetic species inside the film. An important conclusion from these observations is that, although the direct or indirect elimination of the PPV precursor films by MWR may take a few hours to occur, an MW-induced plasma discharge may fully eliminate the film in a few minutes, certainly less than 30 min, a much shorter time than by the normally used thermal process.

CONCLUSION

We have been able to induce the elimination reaction of poly(phenylene–vinylene) precursors into the fully eliminated PPV chain using MW radiation. Some specific conditions were met that allowed the process to be performed in a reasonably short time, especially when compared to the purely thermal elimination method. It is apparent from our results that various different types of mechanisms are contributing to the elimination process, including a small contribution due to some direct interaction of the polyelectrolyte films with the MWs, because of

the presence of water, and an indirect heating of the film because of the interaction between the bulky glass container and the MW field. Besides these basic coupling conditions, other factors, like the specific heat and thermal conductivity of the polymer samples, may have contributed to the temperature increase during the irradiation step. The fact that the samples were placed under vacuum also helped the evaporation process of the volatile species generated during the heating, more specifically, HCl and tetrahydrothiophene.

Our preliminary results with the inclusion of magnetic species inside the polymer precursor seem also to be another way to improve the efficiency of the MW-induced elimination process. It may also offer the interesting possibility of a rapid, simultaneous elimination and doping if the correct oxidizing agent is chosen. It is also clear that an MW-induced plasma, generated inside the sample container, may drastically reduce (to the few minutes) the elimination time required to form the fully conjugated PPV from the polyelectrolyte precursors.

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