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A study of the thermal elimination reaction in a poly(*p*-phenylene vinylene) precursor

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Abstract

Poly(*p*-phenylene vinylene) (PPV) and its derivatives have recently received considerable attention in the field of electroactive organic materials chiefly because of their potential to replace the standard inorganic semi-conducting materials in light-emitting devices. Currently efforts are being made to reduce the carbonyl and hydroxyl defects in these materials which act as quenching sites for the injected charge. Thus, the understanding of the origin of these defects in PPV is extremely important in order to improve its electroluminescence efficiency. These defects are found to appear during the thermal conversion of PPV from its precursor. In this paper we have studied the thermal elimination reaction sequence in a PPV precursor using thermogravimetry and mass spectrometry and the observed results have been associated with standard reaction mechanisms to explain the formation of the aforementioned defects.

Keywords: Defects; Elimination; PPV; TGA; 26009-24-5 (CAS No.)

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1. Introduction

Poly(*p*-phenylene vinylene) or PPV is a conjugated organic polymer with a molecular structure as shown in Fig. 1. The presence of conjugation on the chain backbone imparts many interesting properties such as electrical conductivity [1], photoluminescence [2] and electroluminescence [3] to this polymer.

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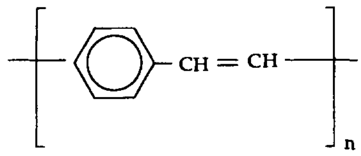


Fig. 1. Molecular structure of a PPV repeat unit.

The synthetic route to PPV as suggested by Wessling and Zimmerman [4] is illustrated schematically in Fig. 2. This scheme produces a water-soluble precursor polyelectrolyte (II) which subsequently undergoes thermal elimination to give PPV (III). The starting material in this scheme has a significant effect on the required elimination temperature which affects the structure obtained and, consequently, the properties of the final polymer. Starting materials with cyclic sulfides, such as tetrahydrothiophene (Ia), are now preferred over materials containing dialkyl sulfides such as dimethyl sulfide (Ib) since the former produces a polymer with a higher level of

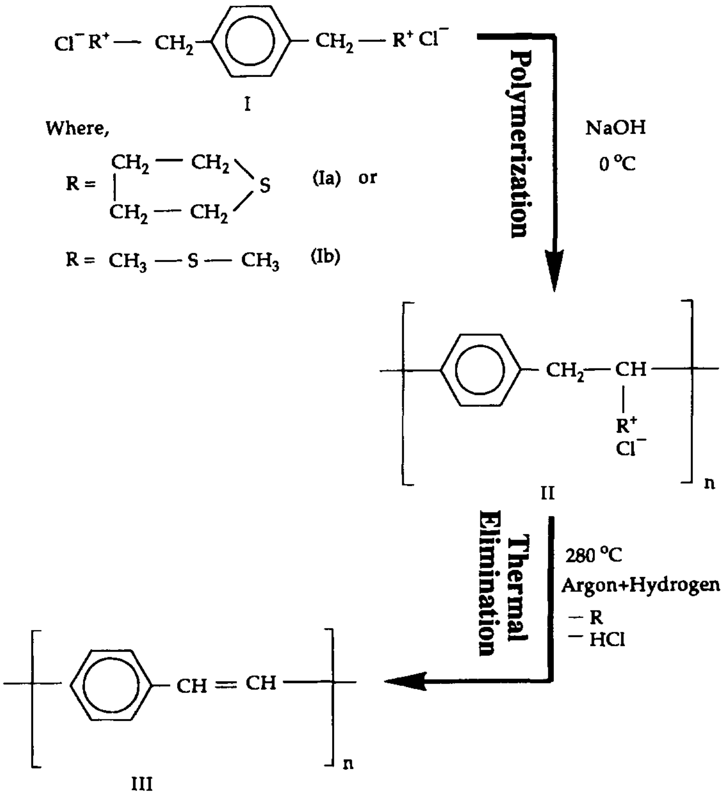


Fig. 2. Schematic diagram showing steps involved during synthesis of PPV via base-induced polymerization.

conjugation. This fact has been experimentally observed by a red shift of the band edge in the polymer IIIa [5] with respect to the polymer IIIb [6] and by the appearance of phonon sidebands in IIIa signifying higher average conjugation length [7]. The polymer IIIa also has another advantage in that it undergoes the thermal elimination reaction at a much lower temperature [7,8].

Thermal elimination reactions have been studied in materials containing cyclic sulfides (type Ia) [9,10] as well as in materials containing dialkyl sulfides (type Ib) [11–15]. However, the reaction is not well understood because of its complex nature, involving several mechanisms, possibly operating simultaneously, thereby making the distinction between the various reaction processes extremely difficult.

In this paper we have examined the thermal elimination reaction in a PPV precursor polymer containing tetrahydrothiophene (IIa) by coupling a standard thermogravimetric analyzer (TGA) to a mass spectrometer (MS) as demonstrated previously for other materials. [16,17].

2. Experimental

Monomer *p*-xylylene bis(tetrahydrothiophenium chloride) was purchased from Aldrich Chemical Company. A basic solution of the required concentration was freshly prepared using sodium hydroxide pellets purchased from Fisher Scientific. Methanol, used as a solvent for the monomer, was also obtained from Fisher Scientific.

Monomer of concentration 0.15 moles (in 50 ml of methanol) was polymerized under an argon atmosphere by a base-induced reaction using an equimolar and equivalent quantity of sodium hydroxide. The reaction was carried out for approximately one hour at 273 K. The polymerization was terminated by adding a slight excess of dilute hydrochloric acid to neutralize any unreacted base. The product was then purified by dialysis using Spectra/Por® cellulose tubing (molecular weight cut-off: 12,000–14,000 daltons). After dialysis the precursor polymer solution was cast into free-standing films by evaporating the solvent under a dynamic vacuum. The free-standing films were found to be transparent, flexible and fluorescent green in color. Detailed descriptions of the above synthesis method are available elsewhere [18–20].

A Seiko Instruments 320 TG/DTA was coupled to a Fisons Thermolab mass spectrometer through a heated silica capillary interface maintaining the temperature of the capillary between 453 and 473 K. The capillary was kept in close contact (2–5 cm) with the TGA pans using a ceramic insert to avoid any heating effects on the sample. The advantage of coupling two or more characterization techniques lies in the fact that the experimental variables such as sample size and shape, ambient atmosphere and flow rate, temperature calibration, and control, heat and mass transfer effects are essentially the same for each technique involved which allows a direct comparison between the results obtained from the coupled techniques.

The PPV precursor sample IIa was examined by heating it from ambient temperature to 823 K at 10 K min in an inert atmosphere of argon inside the TGA sample compartment.

3. Results

Fig. 3 shows the weight loss (TG) and the differential weight loss (DTG) plot of PPV precursor with respect to temperature.

Fig. 4 shows the mass spectrometry (MS) data in the form of total ion intensity (on a logarithmic scale) with respect to time. It should be noted that intensity peaks in the MS plot are not strictly quantitative in nature but are only proportional to the amount of gases evolved since the efficiency of ionization is not known accurately for each ion.

As seen from Fig. 4, the first product to evolve is the water of hydration ($m/z = 18$) which is immediately followed by evolution of tetrahydrothiophene (THT) ($m/z = 88$) and its fragments C_2H_4S ($m/z = 60$), C_2H_2 ($m/z = 26$), etc. This is followed by the liberation of chlorine isotopes ($m/z = 35$ and $m/z = 37$), in the approximately correct ratio of 3:1) which are associated with the elimination of hydrochloric acid. Note that the overlap of $m/z = 37$, arising from the evolution of hydrochloric acid and tetrahydrothiophene elimination, prevents an accurate determination of the chlorine isotope ratio.

Corresponding TG/DTG plots in Fig. 3 show that the weight loss starts at about 373 K with the loss of water. Elimination of THT at about 378 K is evident by a shoulder on the DTG plot. The rate of elimination reaches a maximum at about 421 K, as the DTG plot forms a peak, after which the rate begins to decline. The beginning of chlorine

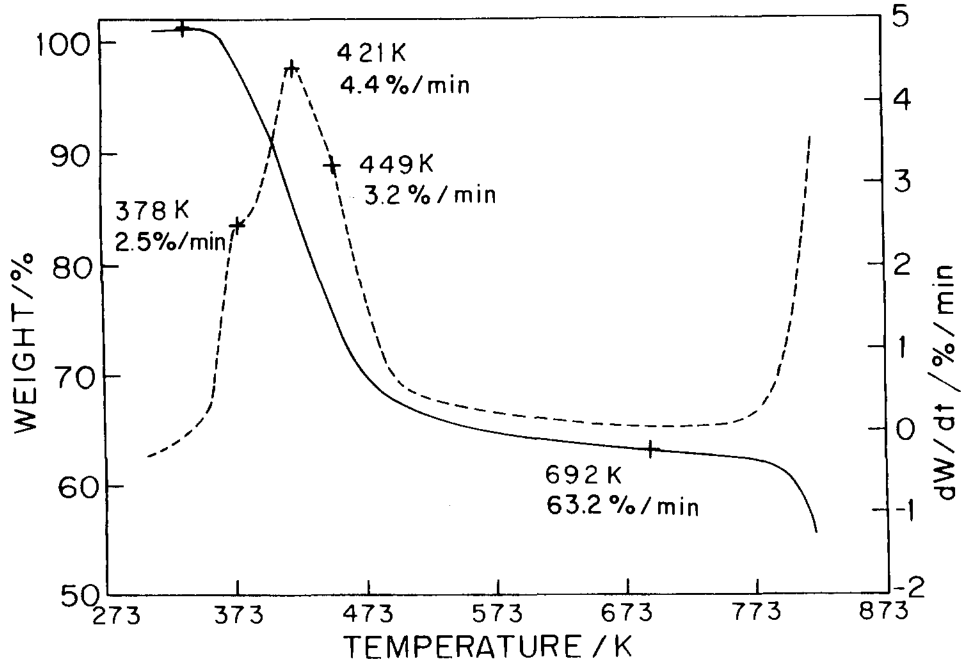


Fig. 3. TG/DTG plot of a PPV precursor from ambient temperature to 773 K at a heating rate of 10 K min^{-1}.

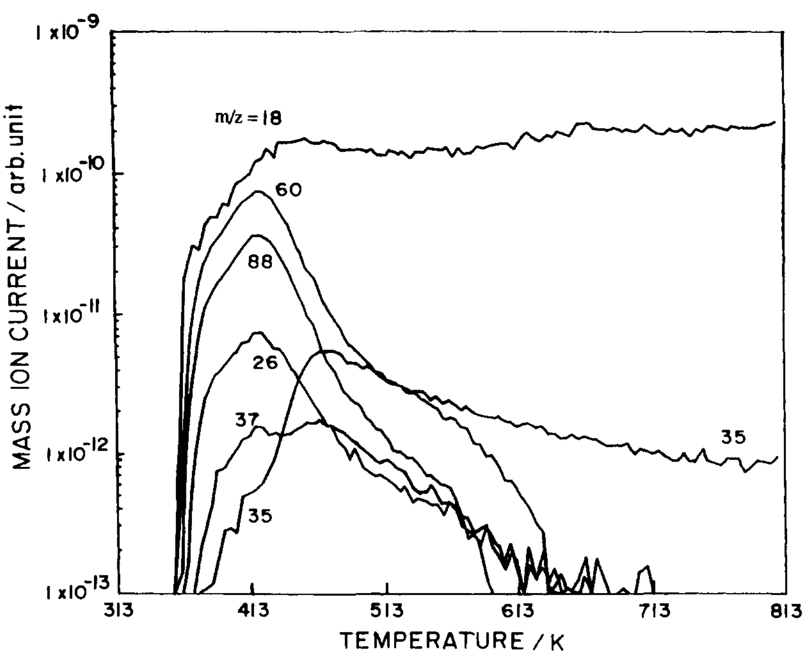


Fig. 4. Mass spectra of evolved products during the thermal elimination reaction in a PPV precursor.

isotope evolution is not clearly observed in the TG/DTG plots as it is superimposed by the THT elimination, but a slight shoulder observed at 449 K, can be linked to the maximum ion current of chlorine isotopes in Fig. 4.

The above results clearly show that the elimination reaction is not a single-step process but involves at least two steps as is confirmed by various authors [9,15]. Therefore, the bimolecular elimination mechanism, E2, can be ruled out for this reaction. Several earlier workers [12–14] proposed an E1cb mechanism for elimination in the IIb precursor but later Halliday et al.[15] suggested an E1 mechanism instead, because the E1cb mechanism was not consistent with the results they obtained. (A detailed description of the standard organic mechanistic pathways, namely, E1, E1cb, E2, etc., can be found in the literature [21,22].)

We believe that the elimination in the IIa precursor, like its predecessor IIb, predominantly follows an E1 mechanism. The MS results clearly show that the first product of elimination is THT which is consistent with the E1 mechanism. Massardier et al. [9] have suggested an alternate route in the IIa precursor which involves the formation of an intermediate product with a C–Cl covalent bond. We believe that such a mechanism, although possible, is very unlikely to occur because such a reaction would ultimately require C–Cl bond cleavage which can occur only at high temperatures, in contrast to our MS result which suggests that chlorine elimination starts at moderate temperatures. The above argument is also strengthened by the fact that almost complete chlorine elimination can be achieved at temperatures of about 553–573 K within a short amount of time [18]. In fact, the formation of a C–Cl covalent bond is considered to be one of the undesirable side reactions in the IIb precursor which leads to a smaller average conjugation length [8] and clearly this is not the case with the IIa precursor. Hence the mechanism suggested by Massardier et al. [9] is probably valid only for IIb type precursors.

However, we believe that the presence of water of hydration affects the elimination mechanism by providing a pathway for a substitution reaction by an S_N1 mechanism. It has been observed that most of the E1 reactions are accompanied S_N1 reactions

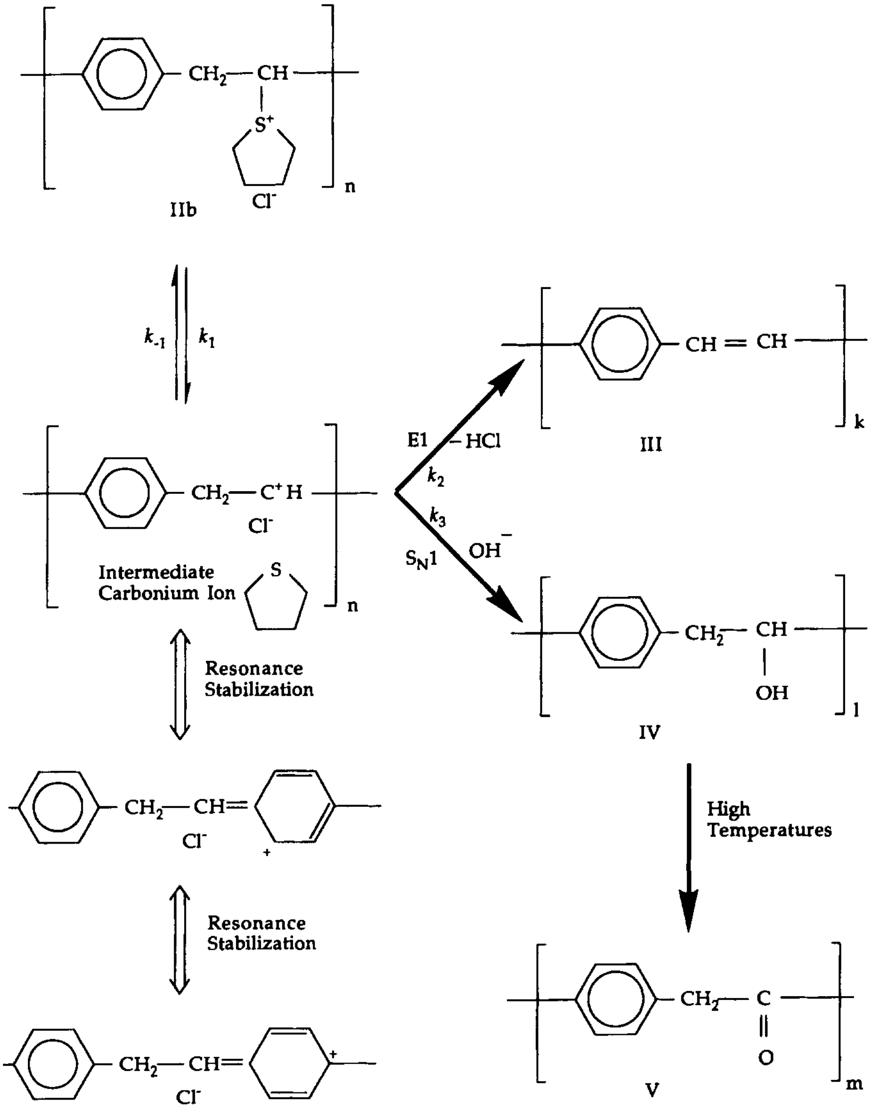
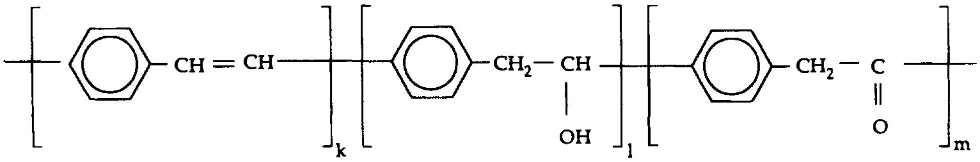


Fig. 5. Proposed thermal elimination reaction sequence in a PPV precursor.



k + l + m = n (average degree of polymerization)

k>>l, m

Fig. 6. Final structure of PPV containing the pure (*k*) and defective (*l,m*) repeat units.

because both the reactions have a common intermediate carbonium ion even though they are converted into different products (elimination and substitution products, respectively).

The reaction sequence we propose, based on our results and observations, is shown in Fig. 5. According to this sequence, mechanism E1 is the prevalent reaction. The intermediate carbonium ion is stabilized by the delocalization of π-electrons on the neighboring aromatic units by resonance effects. This stabilization of carbonium ion minimizes but does not completely eliminate the occurrence of an S_N1 reaction in the presence of water. This competing S_N1 reaction leads to the formation of hydroxyl substituents on some of the units in the final polymer. Also, at high temperatures some of these hydroxyl units are most likely responsible for the formation of carbonyl linkages as suggested by Papadimitrakopoulos et al. [23] As a result the final structure of PPV may be as shown in Fig. 6. The existence of such a structure has been confirmed by IR spectroscopy [18,23].

4. Conclusions

We have proposed a possible thermal elimination reaction sequence in a PPV precursor by employing a combination of thermogravimetry and mass spectrometry. These reactions successfully account for some of the defects, namely carbonyl and hydroxyl, observed in the final polymer.

Acknowledgments

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