Comparing the thermal elimination kinetics of two poly(p-phenylene vinylene) derivative precursors

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Abstract

In the field of conducting polymers, poly(p-phenylene vinylene)(PPV) and its derivatives are objects of much research, particularly for light-emitting diode applications. Due to their insolubility, PPVs are most commonly synthesized from processible precursor polymers by a thermal elimination route. This study focuses on the kinetics of the chlorine precursor route (CPR). The two chlorine precursor polymers of poly (2,3-diphenyl-phenylene vinylene) (DP-PPV) and poly (phenoxy-phenylene vinylene) (PO-PPV) are compared. Both polymers are examined by thermogravimetric analysis (TGA), and experimental data are analyzed using conventional kinetic methods. Activation energies and 60-minute half-life values at various points of thermal conversion (mass loss) are compared. Knowledge of kinetic parameters leads to a better understanding of the CPR and allows prediction of precursor stabilities.

Introduction

Conjugated conducting polymers, commonly referred to simply as 'conducting polymers', are of interest for their high conductivities and optical properties. While intrinsically semi-conducting, upon oxidative or reductive doping these polymers can exhibit conductivity in the metallic regime. Since the discovery of high conductivity in doped polyacetylene in the 1970s,¹ conjugated conducting polymers have been widely studied for their potential applications. Until the discovery of electroluminescence in undoped poly(*p*-phenylene vinylene) (PPV) in 1990,² research in conducting polymers focused on achieving high conductivities. The discovery of electroluminescence shifted the central focus of research in conducting polymers to optoelectronic applications such as organic light emitting diodes (OLEDS).^{3,4} Within the broadening field of conducting polymers, PPV and its derivatives offer the most potential in this application. Despite the current focus, potential applications of conducting polymers are far from limited. Most recently, applications in nanotechnology⁵ and the first reported superconductivity in a conducting polymer⁶ have been seen.

The unique properties of conducting polymers are due to their conjugated backbone. Localized σ -bonds provide structural stability, while delocalized π -bonds result in their semi-conductivity and ability to support charge carriers. Most conjugated polymers, due to their stiff π -bonded backbone, are insoluble in common solvents. Due to their insolubility, many conjugated polymers have proved difficult to process. Synthetic methods, however, have been developed to overcome this problem, and the processibility of OLEDs is an important advantage over conventional LEDs. One common solution to their insolubility is the synthesis of soluble precursor polymers that can be thermally converted to the conjugated conducting polymer. PPV and PPV derivatives can be synthesized from a number of precursor polymers. Various synthetic routes are attractive because the resulting PPVs vary in their electronic, thermal, and optical properties. Three common precursor routes are the xanthate route,⁷ sulfonium route⁸ and the halogen route.⁹ Two precursors of PPV derivatives synthesized via a halogen route, specifically the chlorine precursor route, are of interest in this study. Both thermal elimination reactions are shown below in schemes 1 and 2.

To the extent that PPVs will be used in future optoelectronic device applications, the reaction kinetics of the thermal elimination reaction become important. This kinetics study focuses on the precursor polymers of poly(2,3-diphenyl-phenylene vinylene) (DP-PPV)^{10, 11} and poly(phenoxy-phenylene vinylene) (PO-PPV),¹² and their thermal elimination reactions shown below. In the case of both precursors, the elimination of HCl during heating leads to the formation of the conjugated polymer. Experimental data were obtained on the precursor polymers using thermogravimetric analysis (TGA). A common tool in thermal analysis, thermogravimetric analysis measures the weight change of the sample with respect to temperature and time in a controlled atmosphere. Thermogravimetric data were then used to obtain kinetic parameters of the decomposition step and to estimate precursor polymer lifetimes.



Theory

The analysis of thermogravimetric data was performed using a constant heating rate method developed by Flynn and Wall^{13, 14} and recently standardized.¹⁵ This method is based on the Arrhenius equation which defines the rate constant k as a function of temperature T .¹⁶

Equation 1: $k = A \exp(-E_a/RT)$

Here *R* is the gas constant, *A* is the pre-exponential factor, and E_a is the activation energy characteristic of the reaction. Applying the above equation, Flynn and Wall related the mass fraction volatilized with respect to temperature dC/dT, the heating rate β , and the function of the degree of conversion *f*(C).

Equation 2:
$$\frac{dC}{dT} = \left(\frac{A}{\beta}\right) f(C) e^{-E_{a}/RT}$$

By rearranging equation 2, the following relationship can be obtained.

Equation 3:
$$E_a = \left(\frac{-R}{b}\right) \left(\frac{d \log \beta}{d(T^{-1})}\right)$$

The parameter *b* is constant only if the reaction is first order. The equation can be applied only to reactions that follow first order kinetics. This limits kinetic analysis to the first step in the analysis of a multi-step decomposition. The thermal elimination reactions compared in this work are each first order through a single-step weight loss. In the analysis of various heating rates between 1°C/minute and 9°C/minute, points of equivalent weight loss (percent conversion) can be determined. A plot of these points as log *b* versus T⁻¹ will provide E_a as the slope. The initial values of *b* and E_a are approximate values, which can be improved through an iterative process using successive approximations.¹⁷ Once these values have been determined, the pre-exponential factor and rate constant can be determined. These values can then be used to plot half-life or lifetime with respect to temperature.

Experimental

A TGA 2950 (TA Instruments) was used to collect thermogravimetric data. The two precursor polymers were heated in platinum pans under an inert atmosphere of nitrogen. The samples were heated from ambient temperature, through complete thermal conversion, to 350°C. Heating rates of 2, 3, 5, 7, and 9°C/minute were used. Samples were approximately 5mg. Both precursor polymers were synthesized and provided by Dr. Bing Hsieh, Canon R&D. DP-PPV precursor polymer was in the

form of a light-green powder. PO-PPV precursor polymer was in the form of yellowgreen fluffy mass, which was compacted into pellet form.

Results and discussion

Both thermal elimination reactions occurred via a single step weight loss. An overlay of TGA plots at various heating rates for both the DP-PPV and PO-PPV chlorine precursors are shown in Figures 1 and 2, respectively. The observed weight loss of ~11% in the DP-PPV precursor agrees with the theoretical loss of HCl (12.5%). The PO-PPV precursor as synthesized had undergone 18% conversion to PO-PPV. The observed weight loss of ~12-13% in the PO-PPV precursor agrees with the theoretical loss of HCl from 18% converted PO-PPV precursor (13.3%).

Figure 1: Thermal elimination of the DP-PPV precursor at ramp rates of 2, 3, 5, 7, and 9 (°C/minute), increasing from left to right.





Figure 2: Thermal elimination of the PO-PPV precursor at 2, 3, 5, 7, and 9 (°C/minute), increasing from left to right.

Analysis of the experimental data, as described in theory above, was performed using a TGA Kinetics Program(TA Instruments). An analysis range of 75°C-325°C, encompassing the entire weight loss step, was chosen for all kinetics analyses. Conversion levels of 1, 2, 5, 10, 15, 20 and 25% were chosen. Points of equivalent weight loss at these specific conversion levels are displayed in the common thermograms below (see Figures 3 and 4).



Figure 3: DP-PPV precursor thermograms at ramp rates of 2, 3, 5, 7, and 9 (°C/minute), increasing from left to right.

Figure 4: PO-PPV precursor thermograms at 2, 3, 5, 7, and 9 (°C/minute), increasing from left to right.



The equivalent weight loss points were then plotted as the log of the heating rate versus inverse absolute temperature for each conversion level. The slope of the best-fit lines plotted in Figures 5 and 6 provide approximate activation energy values at each conversion level. Accurate values obtained by successive approximations are

listed in Tables 1 and 2, along with the log of the pre-exponential factor and 60 minute half-life temperatures.





Figure 6: PO-PPV precursor thermograms at 2, 3, 5, 7, and 9 (°C/minute), increasing from left to right.



Conversion (%)	Activation Energy (kJ/mol)	Log (pre-exponential factor) (min ⁻¹)	60-minute half-life temperature (°C)
1	224.5	24.33	173.3
2	208.2	22.07	179.8
5	200.2	20.80	186.8
10	202.9	20.89	191.3
15	208.0	21.32	193.9
20	215.5	22.05	196.0
25	222.5	22.74	197.7

Table 1: : DP-PPV Precursor.

Table 2: :	PO-PPV	Precursor.
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Conversion (%)	Activation Energy (kJ/mol)	Log (pre-exponential factor) (min ⁻¹)	60-minute half-life temperature (°C)
1	112.2	11.45	164.8
2	117.4	12.04	165.4
5	111.4	11.26	167.8
10	115.0	11.63	169.6
15	117.8	11.90	171.6
20	119.9	12.09	173.4
25	121.5	12.22	175.0

Conclusions

The values tabulated above compare the two chlorine precursors (schemes 1 and 2) and indicate that the PO-PPV precursor is less stable. This is indicated by lower activation energies and 60-minute half-life temperatures at each conversion level. Although small conversion levels such as 1% and 2% often involve some initial volatilization of solvent or adsorbed water, in both cases the values are fairly consistent across the range of conversion levels. This indicates that the same mechanism of decomposition is occurring throughout the thermal elimination. The kinetic parameters at a conversion level of 5% can be chosen as representative of each precursor polymer. Both precursors are stable at room temperature, with approximate half-life values for the PO-PPV precursor on the order of hundreds of years, and for the DP-PPV precursor on the order of thousands of years. It may be postulated that the relative instability of the PO-PPV precursor is due to the electron donating effects of the phenoxy substituent. These effects may lead to a more stable

conjugated polymer in the case of PO-PPV, which would result in lower activation energy necessary for thermal conversion. Regardless of the nearly two-fold difference in activation energy, the stabilities of both precursors allow an extended shelf life.

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