Material characterisation

Thermogravimetric study of the kinetics of formation of poly(\textit{para}-phenylene vinylene) by thermal conversion of a sulfonium precursor

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Poly(\textit{p}-phenylene vinylene) (PPV) conjugated polymer films were prepared by thermolytic conversion of poly(\textit{p}-phenylene (tetrahydrothiophenium)ethylene chloride) precursor films, at different temperatures. The reaction kinetics was investigated by isothermal thermogravimetry. Each conversion temperature was found to be associated with an asymptotic value of mass loss. A mathematical analysis relating molar conversion to asymptotic mass loss was derived. The activation energy for dehydrochlorination of the poly(\textit{p}-phenylene chloroethylene) intermediate was found to be $59 \pm 7 \text{ kJ mol}^{-1}$, significantly lower than that for the dehydrochlorination of poly(vinyl chloride) (PVC). The reaction order, on the other hand, was nearly first-order, similar to that for PVC. Film processing conditions that gave conjugated polymer films free of carbonyl defects were identified.

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1. Introduction

Conjugated polymers have been extensively studied for applications in photovoltaic (PV) devices, organic light emitting diodes (OLEDs) and organic thin film transistors (OTFTs) [1]. Poly(\textit{p}-phenylene vinylene) (PPV) is among the earliest prepared conjugated polymers, successfully used in the fabrication of OLEDs [2]. The sulfonium precursor route (the Wessling–Zimmerman route), wherein a poly(\textit{p}-xylenene-\textit{\alpha}-dialkylsulfonium halide) precursor, synthesized from an \textit{\alpha},\textit{\alpha}'-bis(dialkylsulfonium) salt, is thermolytically converted to the PPV conjugated polymer, is commonly used in the synthesis of PPV [3,4].

The synthesis of PPV using the precursor route is a well-documented procedure. The thermal conversion is generally carried out at a temperature in the range of 150 °C to 300 °C. However, carbonyl formation, leading to decrease in the degree of conjugation, is a lingering problem. Okuzaki et al. [5] found significant infrared absorption due to C=O groups in films reacted in ambient air. In another study, partially converted films, obtained by heating the precursor film between 160 °C and 210 °C under nitrogen, were found to have higher photoluminescence and electroluminescence efficiencies than a fully converted PPV, prepared by heating the precursor under vacuum to 300 °C [6]. Papadimitrakopoulos et al. [6] have attributed the lower efficiency to the formation of carbonyl defects in the films heated at higher temperatures.

In our efforts toward synthesizing defect-free films of PPV, we were unable to find information on the effect of
temperature on the kinetics of conversion of the sulphonium precursor to PPV polymer. We, therefore, undertook a systematic thermogravimetry (TG) based kinetic study of the reaction at different temperatures, and correlated the chemical structure of the resulting polymer with the conversion temperature using FTIR spectroscopy. The process developed in the present work resulted in films with negligible carbonyl defects.

TG has been previously used to study solid-state reactions of several vinyl and vinylidene polymers [7–12], such as poly(vinyl chloride), poly(vinyl bromide), poly(vinyl fluoride), poly(vinylidene chloride), poly(vinylidene fluoride) and poly(vinyl acetate), and thermal stabilities of polyesters [13,14], polyurethanes [15], polyimides [16] and nanocomposites based on conjugated polymers [17], poly(styrene and polyhedral oligomeric silsesquioxane (POSS) hybrids [18], functionalized-polyethylenes [19], poly(vinyl alcohol) [20] and phenolic resins [21].

Studies directed toward the determination of the activation energy and reaction order parameters [8,13,19] generally use non-isothermal reaction kinetics, based on the early reports of Freeman and Carroll [22], and Coats and Redfern [23], involving acquisition of mass loss vs. temperature data at a constant heating rate. Measurements at different heating rates have also been used to calculate the activation energy of the reaction [15,22,24]. All of these non-isothermal techniques rely on a constant heating rate, and any deviations from the linear temperature profile due to endo- or exo-thermic reactions [23], or a time lag between the sample temperature and the set-point temperature during temperature ramp, can lead to errors.

We present herein a method to determine the temperature-dependent kinetics of thermal elimination reaction of a tetrahydrothiophenium PPV precursor using isothermal TGA data. To our knowledge, there are few reports on the kinetics of formation of PPV using the precursor route.

2. Theory: kinetic analysis of TG data

2.1. Non-isothermal kinetics

The following derivation is along the lines of the Coats and Redfern analysis [23]. For an n-th order reaction, the rate of reaction may be expressed as:

\[ \frac{d\alpha}{dt} = k(1-\alpha)^n \]  (1)

where \( \alpha \) is the fraction of the polymer mers that have reacted at time \( t \), and \( k \) is the rate constant given by the expression

\[ k = A e^{-E/RT} \]  (2)

where \( A \) is the frequency factor and \( E \) is the activation energy.

If the heating rate is constant, \( \beta [K \ min^{-1}] \):

\[ \beta = \frac{dT}{dt} \]  (3)

Eqs. (1), (2), and (3), can be combined, rearranged, and integrated to get:

\[ \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A T}{\beta} \int_0^T e^{-E/RT} \,dT \]  (4)

For \( n \neq 1 \), the solution of this equation is [23]:

\[ \ln \left( \frac{(1-\alpha)^{-n} - 1}{T^2} \right) = \ln \left( \frac{AR}{n-1} \right) + \ln(n-1) - \frac{E}{RT} \]  (5)

and when \( n = 1 \),

\[ -\ln(1-\alpha) = \ln \left( \frac{AR}{n-1} \right) - \frac{E}{RT} \]  (6)

For most values of \( E \) and the temperature range over which reactions generally occur, the expression \( \ln \left( \frac{AR}{n-1} \right) \) is essentially constant [23], so that, for a correctly chosen value of \( n \), the plots of the expressions on the left hand side of Eq. (5) or Eq. (6) against \( 1/T \) is a straight line of slope \( -E/RT \).

2.2. Isothermal kinetics

For a constant value of \( k \), Eq. (1) can be directly integrated to obtain:

\[ \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \int_0^t k \,dt \]  (7)

For \( n \neq 1 \), the solution of this integration can be written in the form:

\[ \frac{(1-\alpha)^{-n} - 1}{n-1} = kt \]  (8)

and for \( n = 1 \):

\[ -\ln(1-\alpha) = kt \]  (9)

From Eqs. (2) and (8),

\[ (1-\alpha)^{-n} - 1 = At(n-1)e^{-E/RT} \]  (10)

and

\[ \ln \left( \frac{(1-\alpha)^{-n} - 1}{T^2} \right) = \ln(At(n-1)) - \frac{E}{RT} \]  (11)

For the correct value of \( n \), and for conversions, \( \alpha \), determined at a fixed time, \( t \), for reactions at different temperatures, a plot of \( \ln((1-\alpha)^{-n} - 1) \) vs. \( 1/T \) would be a straight line of slope \( -E/RT \). Similarly, when \( n = 1 \), the plot of \( \ln \left( -\ln(1-\alpha) \right) \) vs. \( 1/T \) would be linear with slope \( -E/RT \). Eq. (11) was used in the present study to determine the reaction order and activation energy for the formation of PPV.

3. Materials

p-Xylylene dichloride (CAS no. 623-25-6, MW 175.06 g mol\(^{-1}\), Alfa Aesar, 98%), tetrahydrothiophenium (CAS no. 110-01-0, MW 88.17 g mol\(^{-1}\), Alfa Aesar, 98%), poly(vinyl chloride) (PVC, CAS no. 9002-86-2, \( M_n \) 47,000 g mol\(^{-1}\), \( M_w \) 247,000 g mol\(^{-1}\), Alfa Aesar, 98%) and triethylamine (CAS no. 61-79-7, MW 85.14 g mol\(^{-1}\), Alfa Aesar, 98%) were used in the present study.
80,000 g mol\(^{-1}\), Sigma-Aldrich), pentane (CAS no. 109-66-0, J. T. Baker, 98%), acetone (CAS no 67-64-1, J. T. Baker, ACS reagent, 99.9%), methanol (CAS no 67-56-1, Fisher Scientific, ACS reagent, 99.9%), sodium sulfate (CAS no. 7757-82-6, Sigma-Aldrich, ACS reagent, anhydrous, >99%) were used as received. Ultrahigh purity nitrogen (Airgas, 99.999% purity, <1 ppb oxygen and water) and deionized water were used for all experiments.

4. Experimental

4.1. Polymer synthesis

The reactions used in the synthesis of the precursor polymer, poly\(\left[p\text{-phenylene (tetrahydrothiophenium) ethylene chloride}\right]\) (PPTHTEC, 1), and the conjugated polymer, poly\(\left[p\text{-phenylene vinylene}\right]\) (2), are depicted in Scheme 1 [3,25,26]. Details on the synthesis of PPTHTEC are given in Appendix A. Thermal elimination reaction on PPTHTEC results in the formation of the copolymer shown in the reaction scheme. Stoichiometric conversion of the precursor polymer would yield the PPV homopolymer.

4.2. Intrinsic viscosity measurements

The intrinsic viscosity of the polymer solution was determined using an Ubbelohde viscometer (Canon, B402 0C). A mixture of methanol and water (1:4 volume ratio), containing 50 mM sodium sulfate, was used as the solvent. Solutions of concentrations ranging from about 0.05 g dL\(^{-1}\) to 0.21 g dL\(^{-1}\) were prepared and their elution times through the capillary of the viscometer (that was immersed in a constant temperature bath at 25 °C), were determined.

4.3. Thermogravimetry

TG of the polymer films was performed using a PerkinElmer Pyris 1 Thermogravimetric Analyzer. The films were obtained by solution casting of the dialyzed polymer solution in a polystyrene petri dish and drying in a vacuum oven at 60 °C for 12 h. The sample was heated in a Pt pan under nitrogen purge (20 cm\(^3\) min\(^{-1}\) at standard ambient temperature and pressure, SATP), at a constant heating rate of 20 °C min\(^{-1}\), from 30 °C to 800 °C, to obtain the mass loss TG data. The isothermal TG experiments were performed by heating the sample to a given temperature (in the range of 100 to 250 °C), at a rate of 20 °C min\(^{-1}\), and holding it at this temperature for 120 min.

4.4. Infrared spectroscopy

The IR spectra of thin films of the polymers were collected using a Spectrum 100 Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer, Waltham, MA). A film of the precursor polymer was cast on a polystyrene petri dish, dried in a vacuum oven at 60 °C for 12 h, peeled off from the substrate and mounted between two aluminum windows. The conversion was carried out in a custom-built, air-tight reactor that contained a temperature-controlled heating stage. The stage was first heated to the reaction temperature. The sample was quickly mounted on the stage and the reactor was sealed. Nitrogen was purged through the reactor for 10 min, after which the reactor was evacuated to a pressure of about 10 mmHg using a PTFE dry vacuum pump. Heating of the film was continued for an additional 50 min.

5. Results and discussion

5.1. Synthesis of PPV films

Of the different methods available for the synthesis of PPV [27], the sulfonium precursor approach was selected...
for the present study because it is known to give high molecular weight polymers at high reaction rates and yields. The PPTHTEC polymer, synthesized using a slight variation of the procedure reported by Lenz and co-workers [25,26], was found to have an intrinsic viscosity of 4.94 dL g\(^{-1}\) in a water-methanol solvent blend (4:1 vol. ratio) containing 50 mM Na\(_2\)SO\(_4\) (see Fig. 1). This value of intrinsic viscosity indicates a fairly high molecular weight that is higher than the polymer synthesized by Garay and Lenz [26], evidently because of the higher monomer concentration used in our reactions (63 mM vs. the concentration of 50 mM used in ref. [26]).

Some conversion of the PPV-precursor was expected to occur even at room temperature [25,28], based on the change in the appearance of the solution of the precursor polymer or the cast film from clear and colorless to fluorescent green (indicating the formation of short conjugated polymer or the cast change in the appearance of the solution of the precursor and another peak at 151 °C). Fractional mass loss, \(\frac{m}{m_0}\), of the sample was then maintained at temperature \(T\), evidently due to thermal degradation of the PPV polymer.

### 5.2. Thermogravimetric analysis of reaction kinetics

Fig. 2 shows the TG and differential thermogravimetry (DTG) plots of the PPTHTEC film. A decrease in mass, starting at around 75 °C was observed in the TG plot. The DTG plot showed a peak in the rate of mass loss at 100 °C, and another peak at 151 °C. These peaks are attributed to the conversion of the precursor polymer to PPV, by loss of tetrahydrothiophene and hydrogen chloride. A plateau value of mass loss was reached by about 300 °C, indicating complete conversion of PPTHTEC to PPV. A further decrease in mass was observed beyond about 400 °C, with peaks at 543 °C and 576 °C, evidently due to thermal degradation of the PPV polymer.

Fig. 3 shows mass loss vs. time when films of PPTHTEC were heated at different temperatures. The temperature of the sample was raised to the reaction temperature, \(T\), at a rate of 20 °C min\(^{-1}\) (the non-isothermal heating step). The sample was then maintained at temperature \(T\) for 120 min (the isothermal heating step). The time, \(t = 0\), in Fig. 3 corresponds to the start of the non-isothermal heating step. Fractional mass loss, \(f\), was calculated as \(1 - \frac{m}{m_0}\)

where \(m_0\) is the initial mass of the sample in the TGA pan, and \(m\) is the mass at time, \(t\). It is observed that mass loss reaches the maximum value of 34.5% at a temperature of about 200 °C. An increase of reaction temperature to 250 °C did not result in a further increase in mass loss. Because the conversion of PPTHTEC to PPV by thermal elimination is accompanied by the release of tetrahydrothiophene and hydrogen chloride, the mass loss expected upon complete conversion is 46.62%. However, the maximum mass loss observed in the TG experiments was only about 34.5%. The lower mass loss is attributed to the partial conversion of the sulfonium mer to a reaction intermediate, phenylene chloroethylene, even while the sample was dried at 60 °C to remove the solvent used for casting the film.

Thermal conversion of the sulfonium precursor to PPV has been proposed to occur by the two-step E1 elimination mechanism [29]. Using a combination of TG and mass spectrometry, Shah et al. [29] concluded that the sulfonium precursor undergoes a mass loss at 100 °C due to evolution of the water of hydration, a mass loss at 105 °C due to the elimination of tetrahydrothiophene (with maximum rate of evolution at 148 °C). Mass spectrometry further showed a maximum in the rate of evolution of HCl at 176 °C, a temperature at which a shoulder was seen in the DTG plot. Herold and Schwoerer [28], on the other hand, proposed the formation of chloroethylene units by the Sn2 nucleophilic substitution mechanism, wherein the chloride acted as the nucleophile and tetrahydrothiophene as the leaving group. They suggested that the formation of poly(p-phenylene chloroethylene) (PPCE), which started at about 75 °C, was followed by a pyrolytic elimination of hydrogen chloride at \(T \geq 150 °C\), resulting in the formation of PPV. The PPV polymer finally isomerized to the trans conformation at about 175 °C.

On the basis of these studies, it is assumed that the thermal conversion of PPTHTEC to PPV occurs in two steps, depicted in Scheme 2. Shah and Arbuckle [31] argued that PPCE is not formed during the reaction (because no evidence of C–Cl bonding could be found in their transmission

![Fig. 2](image) TG and DTG plots of the PPV-precursor, PPTHTEC; 20 °C min\(^{-1}\) heating rate and 20 cm\(^3\) min\(^{-1}\) N\(_2\) purge.

![Fig. 3](image) Thermogravimetry plots of PPTHTEC at temperatures of 100 °C, 115 °C, 125 °C, 140 °C, 150 °C, 175 °C, 200 °C, and 250 °C, respectively (bottom to top). The plots for 200 °C and 250 °C are almost indistinguishable.
IR spectra). However, the molar mass of intermediate 3, and therefore, the kinetic analysis of the present study based
on gravimetric data, would be the same regardless of whether
the intermediate is a chloride salt of a carbenium species, as
proposed by Shah and Arbuckle [31], or a chloroethylene
derivative, as proposed by Herold et al. [28].

Fig. 4 shows the fractional conversion, \( \alpha_{2h} \), at the end of
2 h of heating at \( T \geq 100 \, ^\circ\text{C} \) that was calculated from
fractional mass loss using Eq. (B.11) derived in the
Appendix. The zero conversion at 100 \(^\circ\text{C} \), as seen in this
plot, is consistent with the assumption that extent of re-
action B in Scheme 2 is negligible at temperatures \( \leq 100 \, ^\circ\text{C} \).
The mass loss at 100 \(^\circ\text{C} \), as observed in the TG data of Fig. 3,
is primarily because of the elimination of tetrahy-
drothiophene via reaction A. Fig. 4 shows that the conver-
sion of the PPV-precursor was essentially complete even at
a relatively low temperature of 175 \(^\circ\text{C} \). Furthermore, from
Fig. 3, it is seen that at 200 \(^\circ\text{C} \), almost the entire precursor
polymer was converted to PPV within about 20 min of heating.

A plot of \( \ln(1 - \alpha_{2h}) \) vs. \( 1/T \) (see Fig. 5) was used to
determine the activation energy, \( E \), and reaction order, \( n \), of the rate equation for the conversion of PPCE to
PPV. The slope of this linear plot (\( r^2 = \text{square of Pearson}
product moment correlation coefficient} = 0.99932) is equal
to \( -E/R \). The activation energy and reaction order were
found to be \( 59 \pm 7 \ \text{kJ mol}^{-1} \) and 1.18, respectively. The
nearly first order kinetics is consistent with the Ei pyrolytic
elimination mechanism [30]. In fact, the plot of \( \ln\left(-\ln(1 - \alpha_{2h})\right) \) vs. \( 1/T \) was also nearly linear (\( r^2 = 0.9885 \)), in
agreement with the first-order elimination reaction,
yielding an activation energy of \( 50 \pm 8 \ \text{kJ mol}^{-1} \). Note that
the E1 mechanism proposed by Shah et al. [29] would also
lead to first-order reaction kinetics. A distinction cannot be
made between the two reaction mechanisms using the
techniques of the present study.

The activation energy for the elimination of HCl deter-
mined in the present study is significantly lower than the
activation energy of 170 kJ mol\(^{-1}\) reported by Shah and
Arbuckle [31]. They used a modulated TGA method,
wherein a steadily increasing but sinusoidally oscillating
temperature program was applied to the sample, to esti-
mate \( E \). However, such a high activation energy implies the
need of rather high temperatures for measurable reaction
rates. In contrast, the elimination of HCl is almost 100%
complete at a temperature of about 200 \(^\circ\text{C} \).

The relation between activation energy and the onset of
mass loss is evident by a comparison with poly(vinyl
chloride). Pyrolytic dehydrochlorination of PVC (to form
polyacetylene) does not occur until the temperature ex-
ceds 200 \(^\circ\text{C} \) [8]. Our TG measurements on PVC using the
same procedure as was used to obtain the data in Fig. 2
showed a degradation onset temperature of 240 \(^\circ\text{C} \).
Jiménez et al. [8] found that the activation energy and re-
action order for thermal dehydrochlorination of PVC were
about \( 167 \pm 18 \ \text{kJ mol}^{-1} \) and \( 0.85 \pm 0.08 \), respectively. Thus,
the activation energy for dehydrochlorination of PPCE,
determined in the present work, was significantly lower
than that for PVC. The presence of phenylene group on the
\( \alpha \)-carbon atom (the carbon atom attached to Cl), in PPCE, is
believed to be the cause of the significantly lower activation
energy [30] that allowed the formation of the conjugated
polymer at lower temperatures than in the case of PVC. A
similar reasoning has been presented by Herold et al. [28].
to explain the moderate elimination temperature for PPCE compared with PVC.

While the features in our TG and DTG plots are in good agreement with previous reports of other researchers [28,29], the water content of the precursor films of the present study were significantly lower, because the films were dried under a dynamic vacuum for 12 h at 60 °C, whereas the films in the previous studies were dried at room temperature. The presence of water in the film during thermal elimination could introduce hydroxyl and carbonyl defects in PPV, attributed to the competing substitution reaction by an SN1 mechanism [29,31]. The precursor films of the present study were dried at a temperature sufficiently high to remove water, but low enough to prevent any significant extent of PPV formation. Furthermore, the elimination reaction was carried out in an anhydrous and oxygen-free environment to minimize carbonyl defects in the film [6]. FTIR studies of films reacted at different temperatures showed fairly low concentrations of hydroxyl and carbonyl groups in the converted films.

5.3. FTIR spectroscopy

Fig. 6 shows the FTIR spectra of the precursor films reacted at temperatures of 60 °C, 160 °C, 200 °C and 250 °C in a N2 atmosphere. The peak at 964 cm\(^{-1}\) is attributed to the C–H out-of-plane bending of the trans-vinylene group [32]. The peak near 3024 cm\(^{-1}\) is from the trans-vinylene C–H stretch. The peaks at 836 cm\(^{-1}\) and 1518 cm\(^{-1}\) are due to the phenylene ring C–H out-of-plane bending and the phenylene ring C=C stretching, respectively. The peak near 556 cm\(^{-1}\) is attributed to the out-of-plane bending of the phenylene ring.

A clear indication of the progress of the elimination reaction is the decrease in the intensities of the aliphatic C–H stretch resonances (arising from the saturated hydrocarbon groups in the polymer) near 2947 cm\(^{-1}\), 2918 cm\(^{-1}\), and 2852 cm\(^{-1}\) [6].

The conversion to PPV was accompanied by an increase in the intensity of the peak at 964 cm\(^{-1}\) due to the formation of the vinylene group. The intensity of the phenylene ring C=C stretching at 1518 cm\(^{-1}\), on the other hand, remained relatively unchanged for films with different conversion levels, as expected.

The peak near 631 cm\(^{-1}\) could be from the C–Cl stretching vibrations in the PPCE intermediate, and the decrease in the intensity of the peak with an increase in the reaction temperature (see Fig. 6) is consistent with the progressive elimination of HCl from this polymer and the formation of PPV.

The IR spectrum of a solution cast film of the PPV-precursor that was dried in a vacuum oven at 30 °C for 12 h showed a strong O–H stretching band, attributed to residual methanol and water of hydration in the film (spectrum not shown). Drying the solution-cast film at 60 °C for 12 h under dynamic vacuum resulted, however, in complete removal of the solvents (see Fig. 6). The removal of water from the film before the thermal elimination reaction is important in avoiding the formation of hydroxyl and carbonyl defects in the PPV film.

When the precursor film that was dried only at 30 °C (and therefore contained significant amounts of water and/or methanol), was reacted at 250 °C, strong peaks at 1597 cm\(^{-1}\) and 1694 cm\(^{-1}\) were observed in the IR spectra (see Fig. 6). These peaks are evidently because of the C=O stretch and substituent perturbations on the absorption intensity of para-phenylene rings, as has been discussed previously [6]. Okuzaki et al. [5] found significant infrared absorption due to C=O groups in films reacted in ambient air. Papadimitrakopoulos et al. [6] found that the intensity of the carbonyl peak increased with an increase in the annealing temperature, over a range of 200 °C to
300 °C. They also found that when the precursor was converted to PPV in forming gas (a mixture of 15% H₂ and 85% N₂), carbonyl group formation decreased significantly. However, the fully converted PPV films of the present study showed the absence of strong C==O resonances in the IR spectra (see Fig. 6).

Herold and Schwoerer observed a peak at 924 cm⁻¹ and attributed it to the hydroxyl groups bonded to the vinyl units, generated during the synthesis of the prepolymer [28]. This peak was also absent in the IR spectra of the present study.

In summary, the FTIR spectra of the films prepared using the procedure reported herein are consistent with the high conversion of PPTHTEC to PPV, with low concentrations of carbonyl and hydroxyl defects.

6. Conclusions

The formation of PPV by the poly[p-phenylene (tetrahydrothiophenium)ethylene chloride] precursor route involves dehydrochlorination of the poly[p-phenylene chloroethylene] intermediate, the activation energy of which was found to be relatively low (about 59 kJ mol⁻¹) by isothermal thermogravimetry at different temperatures in the range of 100 to 250 °C. The reaction was found to be first order with respect to the phenylene chloroethylene substrate, consistent with an Ei or E1 mechanism of elimination. Because of the low activation energy, a conversion of greater than 90% was achieved within 2 h of heating at 175 °C. About 90 mL of pentane (1:2 volume ratio of the reacting mixture to extracting solvent) was then cannulated into the flask, followed by an addition of a 0.1 M aqueous solution of NaOH (30 mL, 3 mmol) with vigorous stirring using a magnetic stir bar to obtain an efficient mass transfer of the tetrahydrothiophene byproduct into the pentane solution. The polymerization was allowed to proceed for 6 h at 10 °C, after which the stirring was stopped and the supernatant (pentane-rich phase) was decanted off. Sodium hydroxide in the aqueous phase was neutralized by adding 0.1 M hydrochloric acid (about 30 mL). Nitrogen was then bubbled through the aqueous methanol phase to remove any residual pentane. The resulting colorless solution of the polymer was dialyzed in water for three days, using Spectra/Por® 1 Dialysis membranes (MWCO 6000 g mol⁻¹ to 8000 g mol⁻¹) to remove unreacted monomer, NaCl, and other low molecular weight compounds and oligomers. The polymer concentration in the final solution after dialysis was found to be 0.5 to 1 wt%.

Appendix B

Relationship between fractional mass loss in TG and molar conversion

The mass, m, of a sample of the polymer film, at any given stage of conversion, is given by:

\[
m = 226.77N_1 + 138.59N_3 + 102.13N_2 \tag{B.1}
\]

where \(N_1, N_2, \) and \(N_3\) are the number of moles of mers 1, 2, and 3, respectively (cf. Scheme 2), and the coefficients are the corresponding molecular weights. Thus, the fractional mass loss, \(f\), measured in TG, is given by:

\[
f = \frac{226.77(N_{1,0} - N_1) + 138.59(N_{3,0} - N_3) + 102.13(N_{2,0} - N_2)}{226.77N_{1,0} + 138.59N_{3,0} + 102.13N_{2,0}} \tag{B.2}
\]

The effect of film processing conditions on its mechanical properties is discussed in ref. [33].

Appendix A

Synthesis of poly[p-phenylene (tetrahydrothiophenium) ethylene chloride]

To a suspension of 7 g (40 mmol) of p-xylene dichloride in 100 mL methanol, 10.58 g (120 mmol) of tetrahydrothiophene was added. The resulting mixture was heated at 60 °C in an oil bath for 72 h, after which the solution was poured into acetone (300 mL) to precipitate the sulfonium salt. The precipitate was filtered and dried thoroughly under vacuum at room temperature to yield 7.8 g (22.2 mmol) of the bis(tetrahydrothiophenium)-p-xylene dichloride salt (CAS no. 52547-07-6, 55 % yield).

Bis(tetrahydrothiophenium)-p-xylylene dichloride (1 g, 2.8 mmol) was dissolved in methanol (15 mL) in a 250-mL round bottom flask fitted with a rubber septum and purged with nitrogen gas. The flask was immersed in a constant temperature bath at 10 °C. About 90 mL of pentane (1:2 volume ratio of the reacting mixture to extracting solvent) was then cannulated into the flask, followed by an addition of a 0.1 M aqueous solution of NaOH (30 mL, 3 mmol) with vigorous stirring using a magnetic stir bar to obtain an efficient mass transfer of the tetrahydrothiophene byproduct into the pentane solution. The polymerization was allowed to proceed for 6 h at 10 °C, after which the stirring was stopped and the supernatant (pentane-rich phase) was decanted off. Sodium hydroxide in the aqueous phase was neutralized by adding 0.1 M hydrochloric acid (about 30 mL). Nitrogen was then bubbled through the aqueous methanol phase to remove any residual pentane. The resulting colorless solution of the polymer was dialyzed in water for three days, using Spectra/Por® 1 Dialysis membranes (MWCO 6000 g mol⁻¹ to 8000 g mol⁻¹) to remove unreacted monomer, NaCl, and other low molecular weight compounds and oligomers. The polymer concentration in the final solution after dialysis was found to be 0.5 to 1 wt%.

\[
f = \frac{226.77(N_{1,0} - N_1) + 138.59(N_{3,0} - N_3) - 102.13N_2}{226.77N_{1,0} + 138.59N_{3,0}} \tag{B.3}
\]

The value of mass loss measured after 2 h at 250 °C, \(f_{\text{max}}\), corresponds to complete conversion to PPV. Therefore, in the final film converted at this temperature, \(N_1 = N_3 = 0\) and \(N_2 = N_{1,0} + N_{3,0}\). Thus,
Using the observation that the maximum fractional mass loss at 250 °C, \( f_{\text{max}} \), was 0.345, Eq. (B.4) can be used to calculate the ratio, \( N_{3,0}/N_{1,0} \), of the initial moles of 3 to 1 in the precursor film, equal to about 4.114. Thus, the precursor film contained about 80.4 mol % of mer 3.

The films reacted at a temperature of 100 °C or higher are expected to contain negligible amounts of the sulfonium mer, 1. All of these mers would have converted to the phenylene chloroethylene mer, 3. Hence, an equation for fractional mass loss of these films at the end of 2 h of heating, \( f_{2\text{h}} \), can be obtained by setting \( N_1 = 0 \) in Eq. (B.3):

\[
f_{2\text{h}} = \frac{226.77N_1 + 138.59(N_3 - N_2) - 102.13N_2}{226.77N_1 + 138.59N_3}
\]

(B.5)

Because of conservation of the total number of moles of mers 1, 2, and 3 in the film, at all times during the reaction,

\[
N_1 + N_2 + N_3 = N_{1,0} + N_{2,0} + N_{3,0}
\]

(B.6)

Using the approximations that \( N_{2,0} = 0 \), and \( N_1 = 0 \) in the films converted at \( T \geq 100 \degree \text{C} \),

\[
N_{3,0} - N_2 = N_2 - N_{1,0}
\]

(B.7)

The substitution of Eq. (B.7) in Eq. (B.5), and division of the numerator and the denominator by \( N_{1,0} \) gives:

\[
f_{2\text{h}} = \frac{88.18 + 36.46(N_3/N_{1,0})}{226.77 + 138.59(N_3/N_{1,0})}
\]

(B.8)

Using \( N_{3,0}/N_{1,0} = 4.114 \), this equation simplifies to:

\[
f_{2\text{h}} = 0.1106 + 0.04575(N_2/N_{1,0})
\]

(B.9)

The fractional conversion, \( \alpha \), is defined as:

\[
\alpha = N_2/(N_{1,0} + N_{3,0})
\]

(B.10)

Therefore, the conversion at the end of 2 h of heating at each temperature, \( \alpha_{2\text{h}} \), can be calculated for reactions at \( T \geq 100 \degree \text{C} \) using:

\[
\alpha_{2\text{h}} = 0.1955(N_2/N_{1,0}) = 4.27f_{2\text{h}} - 0.472
\]

(B.11)

List of symbols

- \( f \): fractional mass loss
- \( f_{2\text{h}} \): fractional mass loss at the end of heating the sample for 2 h
- \( f_{\text{max}} \): maximum fractional mass loss (fractional mass loss at the end of heating the sample at 250 °C for 2 h)
- \( k \): rate constant
- \( \pi \): reaction order
- \( N_1 \): moles of sulfonium mer, 1, in the polymer sample
- \( N_2 \): moles of the phenylene vinylene mer, 2, in the polymer sample
- \( N_3 \): moles of the phenylene chloroethylene mer, 3, in the polymer sample
- \( N_{1,0} \): initial moles of sulfonium mer, 1, in the polymer sample
- \( N_{2,0} \): initial moles of the phenylene vinylene mer, 2, in the polymer sample
- \( N_{3,0} \): initial moles of the phenylene chloroethylene mer, 3, in the polymer sample
- PPCE: poly(p-phenylene chloroethylene)
- PPTHTEC: poly[p-phenylene[1-(tetrahydrothiophenium) ethylene chloride]] (CAS no. 698999-05-2)
- PPV: poly(p-phenylene vinylene) (CAS no. 26009-24-5)
- PVC: poly(vinyl chloride) (CAS no. 9002-86-2)
- \( R \): gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\))
- \( T \): temperature (K)
- \( \alpha \): molar conversion (defined in Eq. B.10)
- \( \alpha_{2\text{h}} \): molar conversion at the end of heating the sample for 2 h
- \( \beta \): heating rate in thermogravimetric analysis (K min\(^{-1}\))

References