



A study of chloro-*p*-xylylene polymerization kinetics using high-vacuum *in situ* differential scanning calorimetry



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ABSTRACT

The polymerization kinetics of chloro-*p*-xylylene in condensed state was studied by *in situ* non-isothermal DSC measurements conducted at different heating rates in the range from 1.1 to 6.3 °C min⁻¹, using a custom-made heat-flux calorimeter integrated into a vacuum vapor deposition polymerization reactor. The total exothermal effect of polymerization reaction ($Q = 71 \pm 9 \text{ kJ mol}^{-1}$) and its temperature range (−140 to −80 °C) were determined. The differential isoconversional method by Friedman was applied for the kinetics analysis. The effective activation energy increases monotonically with the degree of conversion from about 36 to 55 kJ mol⁻¹. Such behavior was associated with transition to diffusion-limited regime of the polymerization reaction. The reaction model $f(\alpha)$ was evaluated using a model-free method based on the use of the compensation effect. The calculated $f(\alpha)$ values were independent on the heating rate and correspond to the second-order reaction model $f(\alpha) = (1 - \alpha)^2$ in the conversion degrees interval of 30–90%.

1. Introduction

Poly(*p*-xylylenes), also known by their trade name as Parylenes, are a class of polymers traditionally synthesized by vapor deposition polymerization (VDP) technique enabling preparation of thin pinhole-free conformal coatings of controlled thickness without solvents or catalysts [1]. These polymers possess a remarkable combination of chemical inertness, excellent barrier properties, high thermal stability, low dielectric constant and good insulation properties which make them promising for numerous engineering applications, e.g. for protective coatings [2–4], biopassivation coatings for medical implants [5,6], coatings for optical systems [7,8], organic semiconductor devices [9,10], MEMS [11,12], etc. Although over 20 types of Parylenes have been developed [13–15], only a few of them are commonly available, i.e. Parylenes N, C, D (unsubstituted poly(*p*-xylylene), poly(chloro-*p*-xylylene) and poly(dichloro-*p*-xylylene), correspondingly), as well as recently commercialized Parylene HT (a fluorinated version of the polymer), and Parylenes A and AM, having amino groups attached to the benzene rings.

The high reactivity of *p*-xylylenes (PX) and low polymerization temperatures make a study of the polymerization mechanism a non-trivial problem. Unsubstituted poly(*p*-xylylene) (PPX or Parylene N) as the first member of the Parylenes family has received maximum attention in the past. Errede et al. [16] studied the polymerization

kinetics of *p*-xylylene in dilute low-temperature solutions (10⁻¹–10⁻² mol l⁻¹) of toluene or hexane. They calculated the activation energy of the chain propagation reaction ($E_p \approx 36 \text{ kJ mol}^{-1}$) and determined that it is a first-order reaction with respect to monomer. The polymerization kinetics of PX in condensed state initiated on heating was studied by *ex situ* non-isothermal DSC measurements with a commercial calorimeter [17] and by *in situ* DSC with a custom made DSC cell integrated into a VDP reactor [18]. The temperature range (−110 to −75 °C) and the total heat effect ($Q = 86 \pm 8 \text{ kJ mol}^{-1}$) of the polymerization reaction were determined. The effective activation energy E_α of the reaction evaluated by Friedman isoconversional method exhibited variation with the degree of conversion α in the range from 30 kJ mol⁻¹ to 50 kJ mol⁻¹ indicating the complexity of the PX polymerization mechanism in condensed state. The initial part ($\alpha < 0.2$) of the E_α vs. α dependence reveals a decrease from about 50 kJ mol⁻¹ to 40 kJ mol⁻¹, probably indicating a larger contribution of the initiation step. In the range from $\alpha = 0.2$ to $\alpha = 0.85$ the activation energy equals $40 \pm 2 \text{ kJ mol}^{-1}$, which is very close to the activation energy of the chain propagation reaction $E_p \approx 36 \text{ kJ mol}^{-1}$ reported for polymerization of *p*-xylylene in low-temperature solutions [16]. At the end of the polymerization reaction ($\alpha > 0.85$) the effective activation energy decreased from 40 to 30 kJ mol⁻¹, revealing a transition from reaction-controlled to diffusion controlled regime. The reaction model $f(\alpha)$ evaluated by a model-free method based on the use of the compensation

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effect [19] was adequately fitted by the Avrami–Erofeev A2 model $f(\alpha) = 2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$ in the conversion degrees interval of 20–80%, indicating possible nucleation and growth mechanism of the *p*-xylylene polymerization reaction in condensed state [18]. However, it should be noted that to perform DSC measurements *ex situ* with a commercial calorimeter, one needs to devacuumize the VDP reactor to transfer the samples with a frozen chloro-PX condensate into a DSC cell. Unfortunately, in this case one cannot exclude completely heating and partial polymerization of the condensate affecting kinetics of the studied process. The discrepancy between results of *ex situ* and *in situ* DSC experiments on polymerization of unsubstituted *p*-xylylene was demonstrated previously and associated with generation of additional radicals during transfer of the samples from the VDP reactor to the DSC cell [17,18].

Poly(chloro-*p*-xylylene) (Parylene C) is another commercially available member of the Parylene series, compared to Parylene N it is modified only by the substitution of a chlorine atom for one of the aromatic hydrogens. The use of this polymer has very strongly increased in the last few years, especially in the medical industry due to its biocompatibility as a coating for stents, cardiac assist devices, surgical tools, electronics and catheters [5,6]. In addition, its glass transition temperature ($T_g = 90^\circ\text{C}$) [20] is notably higher compared to unsubstituted poly(*p*-xylylene) ($T_g = 13^\circ\text{C}$) [21], which makes this polymer promising as a host matrix for the development of hybrid nanocomposite materials [22,23].

Czaplewski et al. studied the effect of number of chlorine atoms and their location in the reactants' structure (aromatic and/or aliphatic) on the reactivity of various chlorine-substituted derivatives of *p*-xylylene by quantum chemical methods [24,25]. These authors demonstrated that *p*-xylylene, 2-chloro-*p*-xylylene and 2,5-dichloro-*p*-xylylene (monomers of Parylene N, C and D, correspondingly) have similar polymerization reactivity and the activation barriers [24]. However, substitution of terminal hydrogen atoms by chlorine atoms reduces reactivity dramatically [25]. Iwatsuki et al. reported that α , α' , α' , 2,5-hexachloro-*p*-xylylene (HCX) can be isolated as yellow crystals, which can be kept without any change at temperature below 0°C , but polymerize slowly at room temperature and the reaction order of this solid state polymerization was reported to be zero [26]. The zero order of this reaction was explained by specifics of the localized reaction zone propagation throughout the reactant [26]. On the other hand, it was shown that the solution polymerization of HCX is the first order with respect to monomer concentration with apparent activation energy of the polymerization evaluated as 34.4 kJ mol^{-1} [26], which is very close to the activation energy of the chain propagation reaction $E_p \approx 36\text{ kJ mol}^{-1}$ reported by Errede et al. for polymerization of *p*-xylylene in toluene [16]. These values are also practically identical to the effective activation energy for solution polymerization of α , α' , α' -tetrachloro-2-cyano-*p*-xylylene, i.e. $E_\alpha = 36.8\text{ kJ mol}^{-1}$ [27]. Based on these observations, the authors suggested that the polymerization mechanism is the same for all these monomers.

In the present work, the chloro-*p*-xylylene (chloro-PX) polymerization kinetics in condensed state was addressed using *in situ* DSC measurements. To the best of our knowledge, no DSC studies of chloro-PX polymerization have been reported to date.

2. Experimental

2.1. Preparation of the samples

Vacuum-deposited chloro-PX condensate samples were formed in a custom-built VDP reactor using classical Gorham method [28]. A vacuum better than 10^{-3} Pa was maintained during deposition. The cyclic dimer (dichloro[2.2]*p*-cyclophane) molecules ($m \approx 300\text{ mg}$) were sublimated at 140°C and then cleaved into reactive monomers in the pyrolysis furnace at 650°C . Subsequently, the monomer vapor was condensed on an aluminum pan in the sample cell of the calorimeter,

which is integrated in the VDP reactor and attached to a liquid-nitrogen-cooled (-196°C) finger. The pan lids were put into the DSC pans in both the sample and the reference cells of the calorimeter. The deposition time was 60 min. After deposition the condensate was heated up to room temperature at a controlled heating rate and the DSC signal was recorded. To evaluate the sample mass, the weight difference between bare aluminum pan and the same pan after chloro-PX deposition and *in situ* DSC experiment was measured using an automatic electric balance (M3, Mettler) with an accuracy of 10^{-6} g . The typical sample mass was about 0.3 mg.

2.2. In situ differential scanning calorimetry

2.2.1. Calorimeter calibration

The DSC cell utilizes the principle of the heat-flux calorimeter. Detailed description of the calorimeter construction can be found elsewhere [18]. Temperature and heat (peak area) calibrations were performed at multiple heating rates over a wide temperature range with indium, gallium (in passivated aluminum pans) and mercury, using a standard procedure [29]. Afterwards, the calculated calibration corrections were extrapolated to the temperature range of the chloro-PX polymerization.

2.2.2. Baseline correction

The DSC curves of the chloro-PX polymerization show a linear behavior before and after the polymerization peak, forming two characteristic linear baselines (cf. Fig. 1 of Supporting Information, for example). These two linear baselines were used to calculate a sigmoidal baseline according to [30] as follows:

$$\Phi_{\text{baseline}} = (1 - \alpha)\Phi_{\text{monomer}} + \alpha\Phi_{\text{polymer}}, \quad (1)$$

where α is the degree of conversion.

2.2.3. Estimation of the apparatus function of the calorimeter

In the heat-flux DSC experiments, the heat flow rate developed in the sample cannot be recorded directly. Instead, it is always measured via the temperature difference between the sample and reference at a certain distance from the sample. Due to the finite thermal conductivity and heat capacity of the heat conductive path between the point of measurement and the sample as well as the temperature gradient within the sample, a smearing of the heat flux is produced.

For simple cases, the DSC instrument can be described as a linear system and the theory of linear response can be applied. The connection between the heat flow rate Φ_r developed in the sample and the measured heat flow rate Φ_m is given by the convolution integral [31]:

$$\Phi_m(t) = \int \Phi_r(t')a(t - t')dt' \equiv \Phi_r(t)*a(t), \quad (2)$$

where $a(t)$ is the impulse response (the so-called apparatus function, or Green's function) of the DSC system, and the star sign denotes the convolution product. The apparatus function $a(t)$ can be derived from the response to a pulse-like [30,31] or a step-like event [32,33].

The impulse response of the DSC instrument depends on the heat capacity and thermal resistance of the sample as well as on the thermal contact between the sample and the pan. That is why for estimation of the apparatus function it is highly desirable to use a material with thermal properties similar to those of the sample under study [34]. In this work, we used polymerization of *p*-xylylene in the so-called “spike-polymerization” regime for producing a pulse-like event (see elsewhere for details [18]). The measured impulse response of the calorimeter (cf. Fig. 2 of Supporting information) was fitted by a sum of two exponential functions [30]:

$$\Delta T(t) = a_1 \cdot \exp\left(-\frac{t}{\tau_2}\right) - a_2 \cdot \exp\left(-\frac{t}{\tau_1}\right), \quad (3)$$

where the time constant τ_1 of $0.5 \pm 0.1\text{ s}$ essentially determines the

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