



Thermal properties of poly(neopentylmethacrylate) thin films deposited via solventless, radical initiated chemical vapor deposition

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ABSTRACT

This paper investigates the thermal properties of thin films of poly(neopentylmethacrylate) (PnPMA) deposited via solventless, radical initiated chemical vapor deposition (iCVD). The effects of monomer to initiator molar ratio (M/I) on deposition kinetics, thermal properties and composition of the film were investigated. The molecular weight and conversion of PnPMA were observed to increase with increasing initiator concentration. Thermal properties of the film stabilized when annealed to 150 °C which was attributed to removal of short-chain molecules acting as “plasticizers”. Gel-permeation chromatography (GPC) studies and non-linear regression analysis of GPC data confirmed these results. M/I had no significant effect on the thermal stability of iCVD PnPMA and we hypothesize that this behavior is primarily due to weak bond linkages formed during polymer chain termination. The activation energy for the final thermal degradation stage of iCVD PnPMA was similar to that of anionically polymerized PnPMA, indicating that the iCVD polymer at this point was primarily composed of stable polymers that degrade through random chain scission.

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1. Introduction

Initiated chemical vapor deposition (iCVD) is a solventless polymerization technique capable of depositing thin organic films in a conformal manner on a variety of substrates [1–3]. Unlike plasma enhanced CVD (PECVD) and parylene CVD, the relatively mild reaction conditions employed in iCVD process enable higher retention of chemical functionality of deposited polymer [4]. Also, results show that iCVD outperforms PECVD in realizing conformal deposition on microstructured surfaces. Thus iCVD of polymers with various chemical groups including amines, fluorophenyls, epoxies and hydroxyls has been demonstrated on various substrate surfaces [4–7]. Combined, these traits make iCVD attractive for depositing polymer thin films for applications like biocompatibility coatings, chemical and biological sensors, selective membranes and drug delivery [8–11].

Although iCVD polymerization involves similar reaction steps as free-radical bulk polymerization, there are some fundamental differences between the two processes [12]. Compared to bulk polymerization, which is mostly a batch process, iCVD is a surface driven, bottom-up, continuous process [13]. The iCVD polymerization initiation reaction happens at the interface between surface adsorbed monomers and initiator radicals arriving from gas phase. The simultaneous polymerization and deposition steps may lead to monomer molecules getting trapped in the matrix of the polymer and significantly alter their physical properties [14]. Monomer inclusion has

previously been reported by Bakker et al., and is also observed here using gel permeation chromatography (GPC) studies [15]. Typically, iCVD films are deposited at lower temperatures (10–40 °C); however they are frequently exposed to higher operating temperatures and it is important to characterize the behavior of these films over a wide temperature range [16–19]. These factors prompt us to investigate the effects of deposition conditions and thermal treatments on properties and stability of iCVD films.

It is well established that the physical properties of polymers such as glass transition temperature (T_g), coefficient of thermal expansion (α) and elastic modulus (E) are a function of film thickness, molecular weight and composition [20]. Among these T_g is the most important and widely studied property since the trend of T_g variation with film thickness and molecular weight can be used to predict the behavior of most other polymer properties [21]. In this work we investigate the thermal properties and thermal stability of iCVD poly(neopentylmethacrylate) (PnPMA) thin films deposited at different monomer to initiator molar ratio (M/I) and study the effects of film composition and thermal anneal on film properties. Initiator concentration can influence the molecular weight, polydispersity, degree of conversion and rate of polymerization reaction and offer means to tune the properties of the polymer film. PnPMA is chosen as a model polymer since it is a linear, non-crosslinked polymer enabling GPC studies to determine their molecular weight and polydispersity.

All iCVD PnPMA films were deposited on silicon wafers with a native oxide to provide a consistent substrate surface. A variety of techniques including thermogravimetric analysis (TGA), thermal analysis-Fourier transform infrared spectroscopy (TA-FTIR) and thermal volatilization

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analysis (TVA) have been demonstrated in literature for studying the thermal degradation of bulk polymer [22–24]. These techniques require several micrograms of sample and are not suitable for analysis of nanometer thick polymer films. In this study spectroscopic ellipsometry was used to characterize the thermal degradation properties of iCVD PnPMA thin films by monitoring the change in film thickness with temperature for a fixed heating rate. Also, spectroscopic ellipsometry was used to evaluate T_g and α of these polymer films as has been previously demonstrated in literature [25–29]. Further, GPC was used to correlate the change in thermal properties to the composition of the film. Thermal stability of iCVD polymer is hypothesized to depend on the mechanism of polymerization and the last section of the report compares the activation energies of decomposition of iCVD and commercial PnPMA polymer films.

2. Experimental section

2.1. Materials

NPMA (Neopentylmethacrylate) >98% and TBPO (*tert*-butyl peroxide) >98% were purchased from SAFC Hitech and used as received. High purity argon >99.99% was used as the carrier gas. Commercial PnPMA with two different molecular weights, $M_n = 20,000$ and $36,000$ and respective PDI of 1.04 and 1.9 were obtained from Polymer Source (Quebec, Canada).

2.2. iCVD polymerization

All iCVD PnPMA films were deposited in a custom built CVD chamber located in the Tokyo Electron Limited research facility at College of Nanoscale Science and Engineering. The chamber design was based on the design described by Chan and Gleason and was scaled-up to deposit films on 300 mm silicon wafers [13]. The chamber was operated under reduced pressure and had a series of resistively heated filaments suspended above a cooled substrate stage. The filaments were heated to 275 ± 10 °C and the substrate was held at 15 °C. Chamber pressure was maintained at 106.65 Pa (800 mTorr). High purity argon was used to carry NPMA and TBPO vapors into the reaction chamber. The flow rates of NPMA and argon were fixed while the flow rate of TBPO was varied to give monomer/initiator molar ratios (M/I) between 2 and 15. All depositions were done on 300 mm silicon wafers with a native oxide surface.

2.3. Ellipsometry

Polymer film thickness was measured using a variable angle spectroscopic ellipsometry instrument equipped with a heat cell (UV-VASE, J.A Woollam Co., Inc., RC2-XI). Data (Δ , ψ) for all samples were measured in the wavelength range 250–1700 nm at an incidence angle of 70° (with respect to normal to the plane of substrate). The experimental data was fitted using the Cauchy model (CompleteEASE, J.A Woollam Co., Inc.) to extract film thickness values. The heat cell (HTC-200, INSTEC Inc.) was constantly purged with nitrogen to prevent condensation of decomposition products. The heat stage frame was cooled by circulating DI water maintained at 15 °C. For the isothermal heating experiments the samples were heated/cooled at 3 °C/min (STC-200 temperature controller, INSTEC Inc.). Temperature cycles were performed as follows: the sample was heated to a desired temperature and held constant for 30 min, after which it was cooled to and held at 25 °C for 15 min. Isothermal studies showed that the change in film thickness after 30 min was negligible. The heating cycles were performed at 100 °C, 150 °C, 200 °C, 300 °C and 400 °C. A typical result from isothermal cycling of iCVD PnPMA is shown in Fig. 1. Thermal properties (T_g , α and decomposition) can be extracted from each temperature on either the heating or cooling cycle. In our experiments

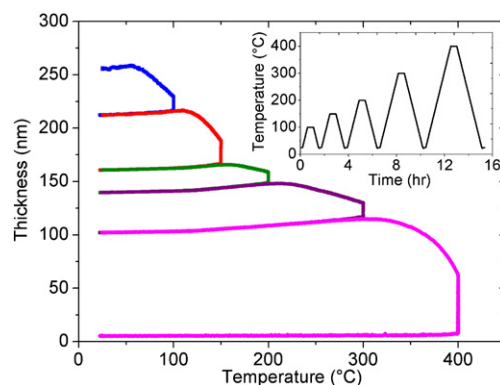


Fig. 1. Change in film thickness for each temperature cycle of iCVD PnPMA films ($M/I = 2$) monitored using ellipsometry. Inset is the temperature profile for the experiment. Heating rate is fixed at 3 °C/min.

we used the cool down cycle for each temperature to extract thermal properties.

The T_g of iCVD PnPMA is obtained by identifying the discontinuity in film thickness vs. temperature. Coefficient of thermal expansion (α) of polymer thin films can be obtained by the equation [25]:

$$\alpha \cong -t_{\text{avg}} \times [d(1/w)/dT] \quad (1)$$

where w is the film thickness, t_{avg} is the average film thickness and T is the temperature measured using ellipsometry. Non-isothermal experiments were conducted by heating the sample at a fixed rate of 5 °C/min from 25 °C to 500 °C. Thermal analysis of commercial PnPMA was conducted by spin-casting polymer dissolved in THF (10% w/v) on a plasma cleaned silicon wafer with a native oxide surface.

2.4. Gel-permeation chromatography

Molecular weight of the polymer was determined by dissolving it in tetrahydrofuran and running the solution through a Styragel HR 3 THF column (7.8×300 mm) attached to a high-performance liquid chromatography system (Waters 1525) equipped with a refractive index detector (Waters 2414). The column was calibrated using polystyrene standards (Fluka 76552) with molecular weight range, M_n 42,000 Da to 435 Da. The GPC data was deconvoluted using non-linear regression analysis with multiple Gaussian fitting. The number of Gaussian curves used for the global fit was fixed based on the number of distinct peaks in the original GPC data. The height and the position of each peak were set as the initial parameters and the Trust-Region algorithm (Matlab 7.10.0) was used in an iterative fashion until the fit converged. The standard square error of the fit was minimized where the R^2 (0.6–0.9) value indicated the goodness of the fit. The fitting constants for each Gaussian were used to plot them individually on the original data for comparison purposes. The area under each Gaussian is calculated using trapezoidal integration method with a spacing of 0.001.

iCVD PnPMA samples deposited with $M/I = 2$, 8.5 and 14.2 representing different zones of deposition kinetics were chosen for studying the thermal properties and composition of the polymer.

3. Results and discussion

3.1. Deposition kinetics

In this study the effect of initiator concentration on deposition rate of iCVD PnPMA was investigated as shown in Fig. 2. All the other parameters including monomer concentration, substrate temperature, chamber pressure, total flow rate and filament temperature were

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