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# Thermal studies on proton conductive copolymer thin films based on perfluoroacrylates synthesized by initiated Chemical Vapor Deposition

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## ABSTRACT

The thermal properties of ion-conductive materials are crucial for their use in temperature-sensitive applications such as polymer electrolyte fuel cells. In this study, 1H,1H,2H,2H,-perfluorodecyl acrylate and methacrylic acid (MAA) copolymers are synthesized by initiated Chemical Vapor Deposition. This method is a solvent-free thin film deposition technique, which allows for the preparation of polymers in distinct stoichiometric compositions. The chemical stability of the copolymers was investigated upon elevated temperatures along with other thermal properties. For this, experimental techniques such as infrared spectroscopy and ellipsometry were used. The data show that samples are chemically stable up to 150 °C, a point above which anhydride formation occurs, resulting in the loss of the conductive groups. A second order thermal transition was found at  $(95 \pm 5)$  °C for polymers containing 20% MAA, which shifts towards higher temperatures as the MAA content increases. In addition, the water stability was tested. While the membranes show considerable water uptake (over 35% at 60% MAA content), mechanical stability is lacking, resulting in rupture formation and partial dissolution. A possible route to overcome this issue is found in crosslinking, with the addition of 15% ethylene glycol dimethacrylate providing sufficient stability to the polymer.

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## 1. Introduction

Membrane materials for application in polymer electrolyte membrane fuel cells (PEMFCs) compete not only for the highest proton conductivities, but have likewise to withstand elevated temperatures and a harsh chemical environment [1]. While some materials such as sulfonated poly(benzimidazole) or poly(arylene ether)s are able to match or even surpass the conductivity of Dupont's Nafion® -the prototypical, commercially available perfluoro-sulfonated ionomer- other requirements, such as hydrolytic stability, remain questionable [2,3]. In the search for easy-to-synthesize and cost-effective alternatives to Nafion, a plethora of different sulfonated compounds have been investigated [4–6]. But also other acid functionalities such as phosphonic [7] and carboxylic acid [8] have been explored for this purpose. Recently, promising conductivity values were reported for thin films of 1H,1H,2H,2H-Perfluorodecyl acrylate (PFDA) and methacrylic acid (MAA) copolymers, synthesized by initiated Chemical Vapor Deposition (iCVD) [9,10]. The iCVD process is a solvent-free technique, operating under mild vacuum conditions and at low substrate temperatures, allowing for conformal polymer deposition even on delicate substrates such as paper [11], pharmaceuticals [12] or reverse osmosis membranes

[13]. The process relies on the thermal decomposition of an initiator (usually a peroxide) at a hot filament (typical temperatures between 200 and 300 °C), thus forming radicals. Monomer precursors, containing vinyl bonds, are delivered as vapors to the sample compartment, adsorbing at the temperature-controlled substrate surface (usually operated between 10 and 60 °C). Radicals from the vapor phase can then react with the vinyl bonds of the adsorbed monomer, turning the initiator-monomer complex into a radical. By further monomer attachment, polymerization is facilitated until chain growth is terminated by another radicalized chain or initiator radical. The selective nature of monomer/initiator interactions in iCVD allows full retention of chemical functionalities as opposed to other deposition techniques like plasma-enhanced Chemical Vapor Deposition, where the carboxylic acid moiety is only partially preserved [14]. In addition, the solvent-free synthesis of copolymers with opposing characteristics (e.g. hydrophilic/-phobic ones) by iCVD is advantageous when compared to standard solution polymerization, where a common solvent and/or multiple processing steps are required [15]. A more detailed description of the iCVD process and of the related fundamental reactions can be found in literature [16,17].

In this study, the thermal properties of iCVD p(PFDA-co-MAA) films are investigated, both under N<sub>2</sub> atmosphere and when fully immersed into water. While the characterization of thermal properties by standard techniques is usually limited to the bulk, spectroscopic ellipsometry readily allows the investigation of materials with thicknesses ranging

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from a few micrometers down to monolayers. For instance, Beaucage et al. studied the glass transition and thermal expansion coefficient of a 300 nm thin polystyrene film by ellipsometry [18]. Another advantage of this technique is that it can be applied to other media than air so that also the swelling behavior of the polymer films can be studied in-situ. Fourier infrared spectroscopy (FT-IR) complements the thermal characterization, allowing insight into the chemical composition and stability of such membranes.

## 2. Experimental details

Radical *co*-polymerization of 1H,1H,2H,2H-Perfluorodecyl acrylate (PFDA, purity 97%) and methacrylic acid (MAA, purity 99%) was performed via initiated Chemical Vapor Deposition (iCVD) in a custom build reactor, using *tert*-butyl peroxide (TBPO, purity 98%) as initiator. For some samples, ethylene glycol dimethacrylate (EGDMA, purity 98%) was added to the process as a crosslinking agent. As substrates, silicon wafers with a native oxide layer (SIEGERT WAFER, Germany) were used. All the depositions were performed at a working pressure of 107 Pa, with initiator and PFDA flow rates being 0.6 and 0.3 sccm, respectively. The MAA flow rates were 2, 4 and 7 sccm for the individual samples. The total flow rate was held at 8 sccm by adjusting the nitrogen patch flow rate accordingly. For the cross-linked samples, the PFDA flow was set to 0.2 sccm while various MAA/EGDMA flow ratios were tested. The filament was heated to 240 °C while the substrate temperature was held at 30 °C. The average layer thickness of the as-deposited polymer films was (220 ± 40) nm. A detailed description of the experimental setup can be found in a recent publication [12]. For comparison, Nafion® 117 thin films (from solution, conc. 5%) were prepared on 2 × 2 cm<sup>2</sup> silicon substrates by spin coating 100 µL solution at a speed of 3000 rounds per minute, resulting in a layer thickness of approximately 220 nm. All materials (unless stated otherwise) were purchased from Sigma-Aldrich, Germany, and used without further treatment.

Transmission mode Fourier transform infrared spectroscopy (FT-IR) was performed on a Bruker IFS 66v/s spectrometer. All the data were converted to absorption spectra in the OPUS software and an automated baseline correction was performed by a custom software written in R, utilizing the algorithms provided in the *baseline* package [19]. Copolymer composition was determined by fitting the experimental data with a linear combination of the respective homopolymer spectra. The fitting parameters are the weighting factors of the homopolymer spectra, which account for their respective fraction in the copolymer.

Spectroscopic ellipsometry measurements were performed with an M-2000 ellipsometer (J.A. Woollam Co., USA) in reflection at an incident angle of 75°, recording optical data in the wavelength range of 370 to 1000 nm. The system was equipped with THMS600 temperature stage (Linkam, UK), allowing for in-situ temperature-dependent studies. Temperature studies were carried out under inert atmosphere, for which a constant Nitrogen flow was applied to the sample chamber. Prior to the measurements, samples were equilibrated by repeatedly cycling them in the (temperature) region of interest (for at least three times), with a hold time of 5 min in-between the cooling and heating cycle. While an irreversible thickness loss occurs during the first cycle(s), three repetitions were found sufficient to equilibrate the samples, i.e. further heating cycles were reversible (in the limit of the experiment). The experimental data were modeled with the CompleteEASE® software, using a three-layer system consisting of the silicon substrate, the interfacial oxide layer and the transparent (polymer) top layer. For the former two, temperature-dependent optical models were taken from literature [20], whereas wavelength- and temperature-dependent refractive indices of the polymers were modeled by the Sellmeier equation. From a non-linear least squares fit of the experimental data, this model yields the optical constants and thicknesses of the polymer layers. For the swelling studies, a liquid cell attachment (J.A. Woollam Co., USA) was used. The data analysis follows the

procedure described above, except for the use of water as the ambient medium in the model.

## 3. Results and discussion

To probe the influence of polymer composition on the thermal characteristics, p(PFDA-*co*-MAA) films, containing different fractions of MAA, were prepared by iCVD. The deposition rate was approximately 20 nm/min and did not change significantly as the MAA content was varied. After deposition, the film thicknesses and the chemical compositions were determined by ellipsometry and FT-IR spectroscopy, respectively. Subsequently, temperature-dependent measurements and swelling studies were carried out in-situ by ellipsometry and finally the chemical composition was reexamined.

### 3.1. Chemical stability by FT-IR

The retention of chemical moieties in the iCVD process and the chemical stability after temperature treatment were assessed by FT-IR spectroscopy. In Fig. 1, FT-IR spectra of films in the as-prepared (dashed line) and in the post heat treatment state (solid line) are shown. Such spectra exhibit mainly two regions of interest. In the so-called fingerprint region, located between 800 and 1300 cm<sup>-1</sup>, the skeletal vibrations of the CH<sub>x</sub> and CF<sub>x</sub> groups are contained. Several different vibrations are overlapping in this region, making a clear distinction between the individual contributions of PFDA, respectively MAA, difficult. However, as the MAA fraction increases, a decrease in the pronounced peak at 1200 cm<sup>-1</sup> is noted. This peak is identified as the symmetric

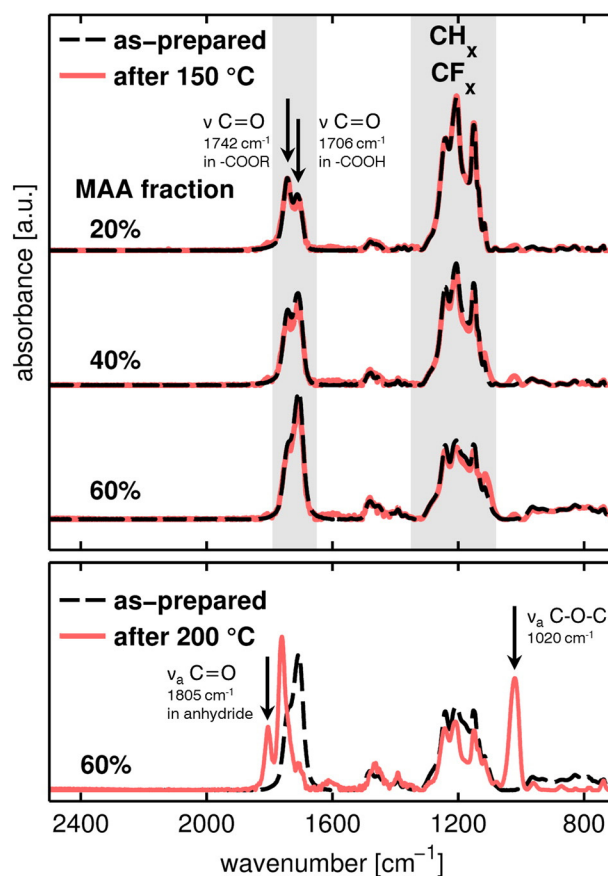


Fig. 1. FT-IR spectra of p(PFDA-*co*-MAA) films in the as-prepared state and after being heated to 150 °C under N<sub>2</sub> atmosphere. The peaks of the ester groups (–COOR) and of the carboxylic acid groups (–COOH) are characteristic for PFDA and MAA, respectively. At the bottom, the spectra of a film containing 60% MAA are shown before and after heating to 200 °C. All data are normalized by the respective sample thicknesses.

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