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Preparation of solution-processable colorless polyamide-imides with extremely low thermal expansion coefficients through an *in-situ* silylation method for potential space optical applications

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Abstract: Several tough and flexible fluorinated polyamide-imide films were prepared from trimellitic anhydride chloride and 2,2′-bis(trifluoromethyl)benzidine through a facile one-pot *in-situ* silylation method. By incorporating fluorinated side groups, the solubility of the prepared polyamide-imide was greatly enhanced. Meanwhile, due to their linear chain configuration and the existence of hydrogen bonding, the prepared polyamide-imide films revealed high tensile strength, high tensile modulus, high glass transition temperature (Tg) and most interestingly, very low coefficient of thermal expansion (CTE) of 11 ppm/°C. Copolymerization with pyromellitic dianhydride (PMDA) led to an extremely low CTE of 4 ppm/°C which should be among the lowest values available for soluble polyamide-imides. The optical homogeneity and stress homogeneity of the obtained polyamide-imide films were also tested. After non-contact with substance and thermal treatment at 300°C, they revealed a better optical homogeneity and stress homogeneity than that of the commercially available Kapton polyimide (PI) films, with a PV value of 0.915 λ and RMS value of 0.163 λ. Thus, these colorless and soluble polyamide-imide films simultaneously possessing promising optical imaging performance are good candidates as novel diffractive membrane optical system architectures.

Keywords: colorless polyamide-imide; low coefficient of thermal expansion; membrane optics; optical homogeneity; synthesis.

1 Introduction

Polyimides (PIs) are a kind of high performance polymer with excellent mechanical properties and thermal stability (1–3). In most of the case, fully imidized PIs with improved solution processability is highly appreciated, thus significant effort has been spent in synthesizing solution processable PIs that still maintain their excellent mechanical and thermal properties by structural modification (4–11). Meanwhile optically transparent high-temperature resistance polymers have great potentials in various optical and optoelectronic applications, thus optically transparent PI with solution processability is of great value (12–17). A recent research topic that has attracted great attention is to develop highly transparent PI materials as an alternative material to fragile/heavy inorganic glass substrates (18–22). For such optical application, the PIs are required to simultaneously possess very high heat resistance (Tg>300°C) and excellent dimensional stability for overcoming the harsh heating/cooling cycle in space environment (CTE<10 ppm/°C), and very high optical and stress homogeneity. However, in most cases, the method that enhanced their solubility generally led to poor dimensional stability.

In order to achieve the combination of desirable properties (solution-processability, colorless and low CTE) in PIs, the introduction of fluorinated groups is a good strategy. The most suitable diamine monomers are probably limited to CF_3-containing 2,2′-bis(trifluoromethyl)benzidine (TFMB) which contains a linear structure that contributes to the low CTE. The CF_3 group also enhances the solubility. Besides, the incorporation of the electron-withdrawing CF_3 group reduces the interchain charge transfer complex and thus leads to colorless PI films. For example, Hasegawa reported an excellent work on fluorinated polyamide-imide using trimellitic anhydride chloride (TMAC) and TFMB (23), the chemically imidized films were almost colorless and soluble in organic solvents, besides, the polyamide-imide film has a high Tg and a considerably low

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CTE of 9.9 ppm/°C, such a combination of desirable properties have rarely been reported. However, the polyamide-imide was synthesized through a time-consuming process where a novel dianhydride containing amide bonding must be synthesized and purified. Direct condensation between TMAC and TFMB led to fragile polyamide-imide films with very poor mechanical properties.

With this in mind, here we report a facile one-pot synthesis of solution-processable colorless polyamide-imides with good mechanical properties and extremely low CTE through an *in-situ* silylation method. Silylation method was first reported for the synthesis of aromatic polyamides by Oishi et al. (24). After that, regarding the water sensitivity and the time-consuming process, an *in-situ* silylation method of aromatic diamines for PI synthesis where trimethylchlorosilane (TMSCl) or other silylated agents were added to the diamine solutions followed by adding dianhydride to fulfill the preparation process was mainly developed by Muñoz et al. (25, 26). With reference to Muñoz et al., these results prompted us to investigate the effect of activation agents in the facile preparation of the above-mentioned polyamide-imide films. Several fluorinated polyamide-imide films prepared from TMAC and TFMB using *in-situ* silylation of diamine TFMB as activated monomer were synthesized. Due to the activation of silylated diamine monomer, all of the one-pot synthesized polyamide-imide films showed excellent mechanical properties. The effects of the base on the molecular weight of the polyamide-imides were investigated systematically. All of the soluble polyamide-imide films possess high tensile strength, high tensile modulus, high Tg and most interestingly, a very low CTE. Membrane optics has attracted more and more attention in recent years, further study showed that the prepared polyamide-imide films revealed a better optical homogeneity and stress homogeneity than that of the commercially available Kapton PI films, thus, these colorless polyamide-imide films with excellent optical imaging performance are good candidates as novel diffractive membrane optical system architectures.

2 Experimental

2.1 Materials

TMSCl, 2,2′-bis(trifluoromethyl)benzidine (TFMB), TMAC, pyromelliticdianhydride (PMDA), N,N-dimethylacetamide (DMAc), N,N-dimethylaminopyridine (DMAP), anhydrous pyridine (Py), triethylamine (Et_3N), isoquinoline (IQ) and other solvents were purchased from Aladdin Industrial Corporation, Shanghai and purified through standard procedure.

2.2 Preparation of polyamide-imide films through an *in-situ* silylation method

A three-neck flask equipped with a mechanical stirrer and a nitrogen in-let and out-let was charged with 10.0 ml of anhydrous DMAc and 10.0 mmol of TFMB, the mixture was stirred at room temperature until all the solids had dissolved. Then, the solution was cooled to 0°C and an equal molar of TMSCl was slowly added to the solution, followed by the corresponding bases. The solution was heated to room temperature and stirred for 15 min to assure the formation of the silylated diamine. After that, the solution was cooled to 0°C, and 10.0 mmol of TMAC was added followed by 10.0 ml of anhydrous DMAc. The reaction mixture was then stirred for 15 min at 0°C and then left to react overnight at room temperature. The chemical imidization was accomplished by using an acetic anhydride (40 mmol)/Py (20 mmol) mixture. The reaction mixtures were stirred at room temperature for 6 h followed by heating for a further 3 h at 60°C to finish the imidization process. The polyamide-imide was precipitated into 1000 ml of methanol and washed several times with methanol to remove traces of solvent. All the polymers were dried overnight under a vacuum at 100°C.

Polyamide-imide films were prepared by dissolving the obtained powders in DMAc in a concentration of 10%wt, the solution was poured onto the glass plate, it was then treated by a standard process of 100°C for 1 h, 200°C for 1 h and 300°C for 1 h, respectively, under vacuum. In order to improve their optical homogeneity, another thermal process was also adopted, the polyamide-imide film preliminarily treated under 100°C for 1 h and 200°C for 1 h under vacuum was peeled off from the glass substrate and the edge of the polyamide-imide film was attached on grommets, the polyamide-imide film was further treated at 300°C for 1 h non-contact with substance (polyamide-imide-G).

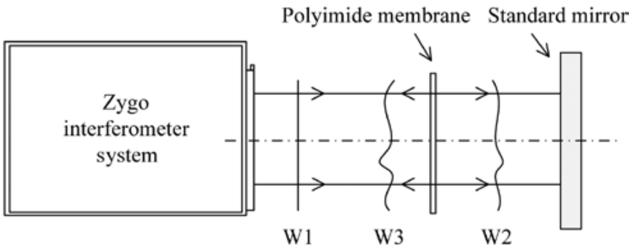
2.3 Characterizations

Fourier transform infrared (FTIR) spectra were measured with a Nicolet 560 spectrometer. The number- (Mn) and weight-average molecular weights (Mw) for PIs were determined by gel permeation chromatography (GPC) using DMF as an eluent at room temperature on a high performance liquid chromatography (HPLC) system with a GPC column and an UV detector at a flow rate of 1 ml/min. The calibration was carried out with standard polystyrenes.

The coefficient of thermal expansion (CTE) was measured by thermomechanical analysis (TMA) in the range of 30–200°C at a heating rate of 5°C/min on a thermomechanical analyzer (Bruker-AXS, TMA 4000) with a fixed load (10 g load for 20 µm thickness) in a dry nitrogen atmosphere. After the preliminary first heating run up to 200°C and successive cooling to room temperature in the TMA chamber, the data were collected from the second heating run to remove any influence of adsorbed water and heating history.

The glass transition temperature, the storage modulus and the energy loss were measured by the dynamic mechanical analysis (DMA) at a heating rate of 5°C/min. The measurements were conducted at a sinusoidal load frequency of 0.1 Hz in a nitrogen atmosphere. The thermal stability was measured using a thermo gravimetric analysis (TGA) instrument (SDT Q600) over the temperature range of 30–800°C with a heating rate of 10°C/min.

The transmission spectra of polyamide-imide films (20 µm thickness) were measured on an ultraviolet-visible-near infrared spectrophotometer (PE Lambda 1050) in the wavelength (λ) range of 200–1800 nm. The light transmittance at 400 nm (T400) was determined from the spectra. The optical inhomogeneity of polyamide-imide film was characterized by a wavefront error using a Zygo laser interferometer with an accuracy of λ/1000 (λ=632.8 nm, λ is the measurement wavelength). The schematic representation of wavefront measuring is shown in Scheme 1. The standard plane-wavefront (W1) emitted by the interferometer going through the optical membrane, optical thickness aberration is modulated onto the plane-wavefront (W2). After being reflected by the standard mirror, W2 transmits through the PI membrane again. The plane-wavefront (W3) interferes with the reference plane-wavefront in the Zygo interferometer system. The peak to valley (PV) and root mean square (RMS) values of the transmission wavefront error are the two common quantitative indicators of optical homogeneity for optical elements.



Scheme 1: Schematic presentation of Zygo interferometer for measuring the optical homogeneity of polyamide-imide films.

The stress homogeneity of polyamide-imide films was measured by an Exicor AT300 birefringence measurement system with an accuracy of 0.2 nm/cm. The measuring principle is based on the photoelastic effect to determine the stress distribution in a material. Upon the application of stresses, photoelastic materials exhibit the property of birefringence. Information such as stress and its orientation can be obtained by analyzing the birefringence.

3 Results and discussion

Several fluorinated polyamide-imide films were prepared using *in-situ* silylated diamine TFMB as an activated monomer. In order to enhance their properties, 20%mol rigid PMDA dianhydride was copolymerized (copolyamide-imide). The successful preparation of PAA precursor and PI films were confirmed by FT-IR and are shown in Figure 1. All the resulting polyamide-imides showed a similar pattern. FT-IR spectra show no trace of amic acid peaks indicating the polyamide-imides were fully imidized. This was also confirmed by the peaks around 1727 and 1781 cm^{-1} ascribed to the stretching of carbonyl group of imide ring and 1369 cm^{-1} of C-N-C stretching of the imide ring.

Previous reports have revealed that in the *in-situ* silylation method, the presence of a base such as pyridine was effective to obtain high molecular weight PIs. So we systematically studied the effect of various bases on the

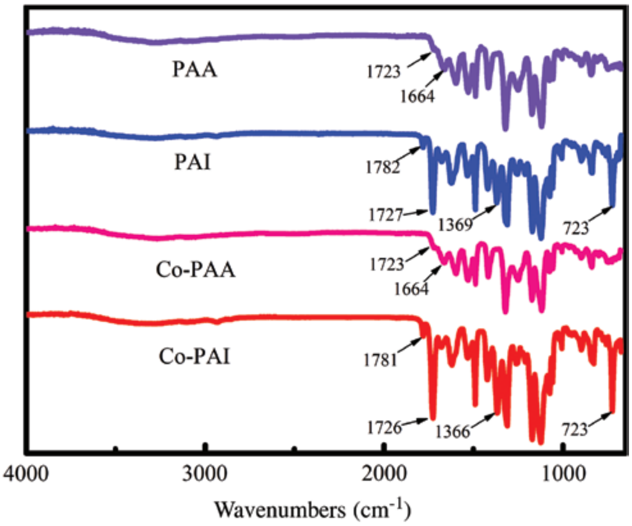


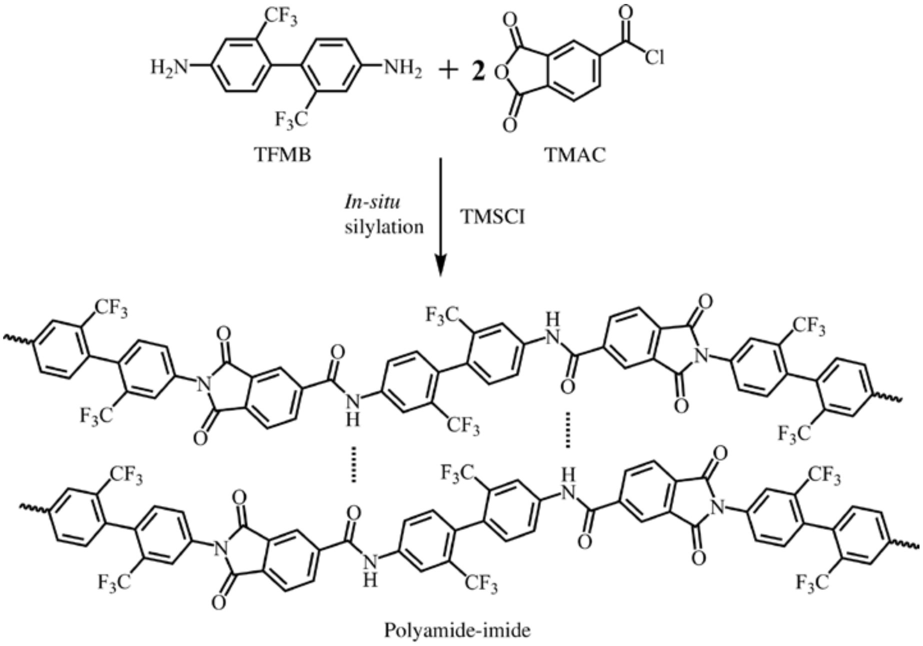
Figure 1: FTIR spectra of polyamide acid precursor and the resulting polyamide-imide films.

molecular weight of polyamide-imides. They are shown in Table 1. Without the activation by TMSCl, polyamide-imide with very low Mw of 25,300 was obtained, and when the TFMB was silylated by TMSCl, a slightly increased Mw of 28,300 was observed. However, if pyridine as an organic base was added, the molecular weight of the resulting polyamide-imide was dramatically increased to 60,600. The use of stronger bases, such as DMAP, Et_3N or IQ together with TMSCl as activating agents, yields a slightly lower molecular weight. However, the use of small amounts (0.1 mol per mole of pyridine) of a strong base DMAP together with pyridine has an excellent conservative active role in the polycondensation reaction, and the highest molecular weights of 75,100 were obtained, and this formula is also adopted as the optimized process for the preparation of high-performance fluorinated polyamide-imide films. In terms of mechanism, the function of the base in the *in-situ* silylation process is favorable for the silylation of the diamine where a high base pK_a is unfavorable. In addition, the base could increase the transfer of electronic density of the silylated amine to the dianhydride moiety which can open the anhydride cycle simultaneously with the elimination of the trimethylsilyl group. Compared with pyridine, the cobase of higher pK_a, DMAP, interacts more strongly with the silicon atom and the trimethylsilyl removal is made easier. Thus, the DMAP/Py synergistic reaction is preferred.

Contrary to the brittle film prepared without activation, the *in-situ* silylation method resulted in tough and flexible polyamide-imide films. Scheme 2 illustrates the linear chain conformation and the interesting interchain hydrogen bonding interaction of TMAC/TFMB polyamide-imide synthesized through the *in-situ* silylation method. The physical properties of the polyamide-imide films

Table 1: Molecular weight of polyamide-imide as a function of various bases.

Samples	Silylating agent	Organic base	Mw	Mn	Mw/Mn
1	None	None	25,300	15,800	1.60
2	None	Pyridine	15,400	13,600	1.87
3	TMSCl	None	28,300	12,000	2.36
4	TMSCl	Pyridine	60,600	21,000	2.89
5	TMSCl	DMAP	37,500	11,700	3.21
6	TMSCl	Et_3N	55,100	35,100	1.57
7	TMSCl	Isoquinoline	49,200	26,200	1.88
8	TMSCl	Pyridine90%+DMAP10%	75,100	44,700	1.68



Scheme 2: Schematic representation of the linear chain conformation and the interesting interchain hydrogen bonding interaction of TMAC/TFMB polyamide-imide.

were characterized by tensile analysis, DMA, TMA and TGA analysis. As demonstrated in Table 2, polyamide-imide films prepared from TMAC and TFMB showed a tensile strength of 159.8 MPa, a tensile modulus of 3.65 GPa, and had a relatively low CTE of 14.7 ppm/°C. When the polyamide-imide film was attached on the grommet, after thermal treatment, the previously mentioned properties were further improved to 172.3 MPa, 4.04 GPa and 11.6 ppm/°C, respectively. In order to further improve their physical properties, a rigid PMDA was copolymerized, the resulting copolyamide-imide revealed similar mechanical properties but a dramatically reduced CTE of 4 ppm/°C, which is almost the same value as inorganic optical glass. Such a low CTE characteristic (i.e. excellent dimensional stability against thermal cycles in space) in addition to high transparency and high Tg make them promising candidates as space optical devices.

Dynamic mechanical analysis is a powerful technique for measuring the thermal mechanical properties of heterocyclic aromatic polymers with very high Tg. The temperature dependence of the dynamic storage modulus and Tan δ of polyamide-imides are shown in Figure 2. The glass transition temperature of films was measured as the peak of the Tan δ curve. The prepared polyamide-imide showed a very high Tg of 335°C and copolyamide-imide with a Tg of 327°C. The thermal stability of fluorinated polyamide-imide was characterized by TGA. The results are given in Figure 2, both of them showed a similar decomposition behavior in the range from 500 to 550°C, and a carbon yield of 50% when heating to 800°C.

The solubility of the prepared polyamide-imides was tested qualitatively to study the improvement of the solubility through the introduction of trifluoromethyl groups, and the results are summarized in Table 3. It shows that the solubility was considerably enhanced. Fully imidized PI generally possesses no solubility in any of these polar solvents, while the prepared fluorinated polyamide-imide films demonstrated excellent solubility in NMP, DMAC, DMF and DMSO, it is even soluble in a low boiling point solvent like THF. The copolymerization of rigid PMDA monomer decreased their solubility; however, it still can be dissolved in DMAc and DMF.

Optically transparent high-temperature resistance polymers have great potential in various optical and optoelectronic applications, thus optically transparency of the synthesized polyamide-imide were studied. As can be seen in Figure 3, the fluorinated polyamide-imide is essentially colorless, as confirmed by the very high light transmittance (T400 nm=15%, T430 nm=80%, T450 nm=86%), in contrast to wholly aromatic commercial PI like Kapton which are T450 nm=0%. Thus, the prepared fluorinated polyamide-imide films were very useful to erase PI film

Table 2: Physical properties of fluorinated polyamide-imide and copolyamide-imide films.

Samples	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	CTE (ppm/°C)
Polyamide-imide	159.8	3.65	15.6	14.7
Polyamide-imide-G	172.3	4.04	13.2	11.6
Copolyamide-imide	166.4	3.59	14.2	4.2
Copolyamide-imide-G	183.6	4.32	12.5	3.8

Table 3: Solubility of prepared fully imidized polyamide-imide films.

Samples	THF	DMF	DMAc	NMP	DMSO
Polyamide-imide	+++	+++	+++	+++	+++
Copolyamide-imide	-	+++	+++	++	-

+++, Readily dissolved; ++, dissolve; +, partially dissolved; -, undissolved. THF, tetrahydrofuran; DMF, N,N-dimethylformamide; DMAc, N,N-dimethylacetamide; NMP, N-methyl-2-pyrrolidone; DMSO, dimethyl sulfoxide.

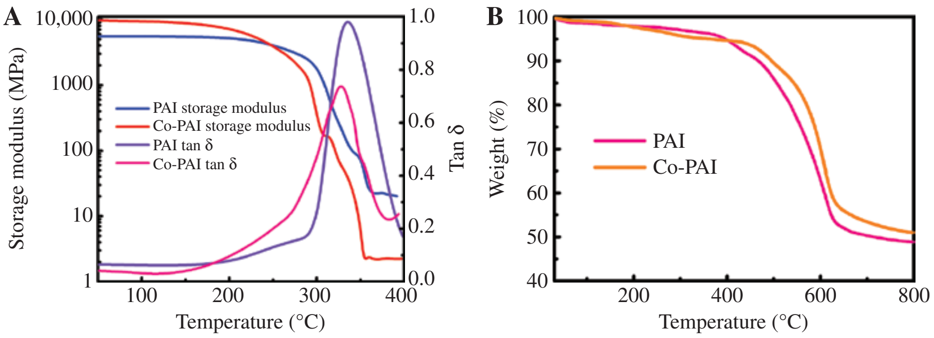


Figure 2: DMA and TG analysis of synthesized polyamide-imide films. (A) The loss tangent tan δ is the ratio of loss modulus and storage modulus. (B) The peak of the Tan δ curve indicates the glass transition temperature.

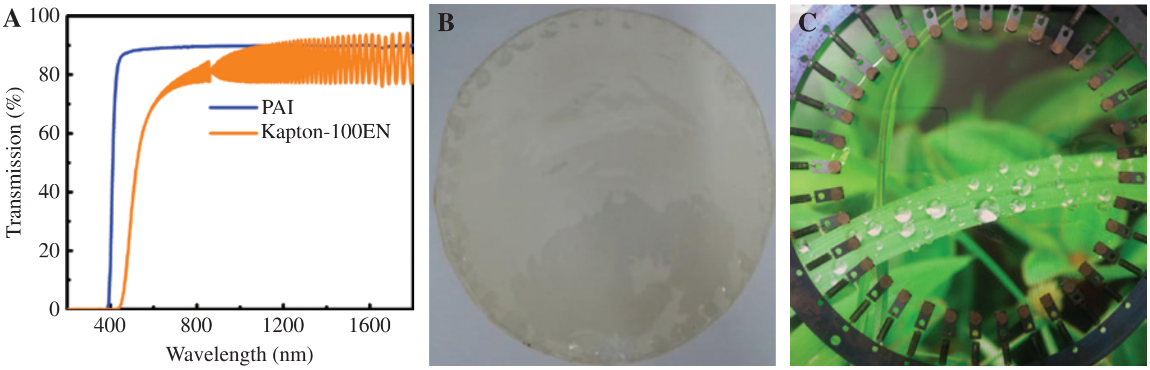


Figure 3: The UV-Vis spectra of fluorinated polyamide-imide and Kapton film (A), and the digital photo of prepared polyamide-imide films in the free state (B) and attached to a grommet (C).

coloration on the basis of inhibited charge-transfer interactions through the introduction of trifluoromethyl groups.

So far, almost all of the research has focused on optical application only characterized their optical transparency of the PI films, however, in order to develop high performance PI films that can be an alternative film to fragile/heavy inorganic glass substrates, only optical transparency is not enough. For such an application, the PIs must possess optical homogeneity and stress homogeneity equal to that of optical glass, and such research is rarely reported. Principally, the optical thickness aberration of membrane caused by the fabrication process, etc., would have a negative modulation effect on the ideal light wavefront, so optical inhomogeneity of the resulted polyamide-imide could be characterized by wavefront errors with the application of the Zygo laser interferometer. The membrane wavefront errors of polyamide-imide film by direct imidization and by suspending on a grommet are shown in Figure 4, respectively. Comparing the wavefront maps and interference fringe maps, it is found that the PV and RMS of wavefront errors are reduced and the interference fringe becomes sparse. Both of the results confirmed that the optical homogeneity can be improved

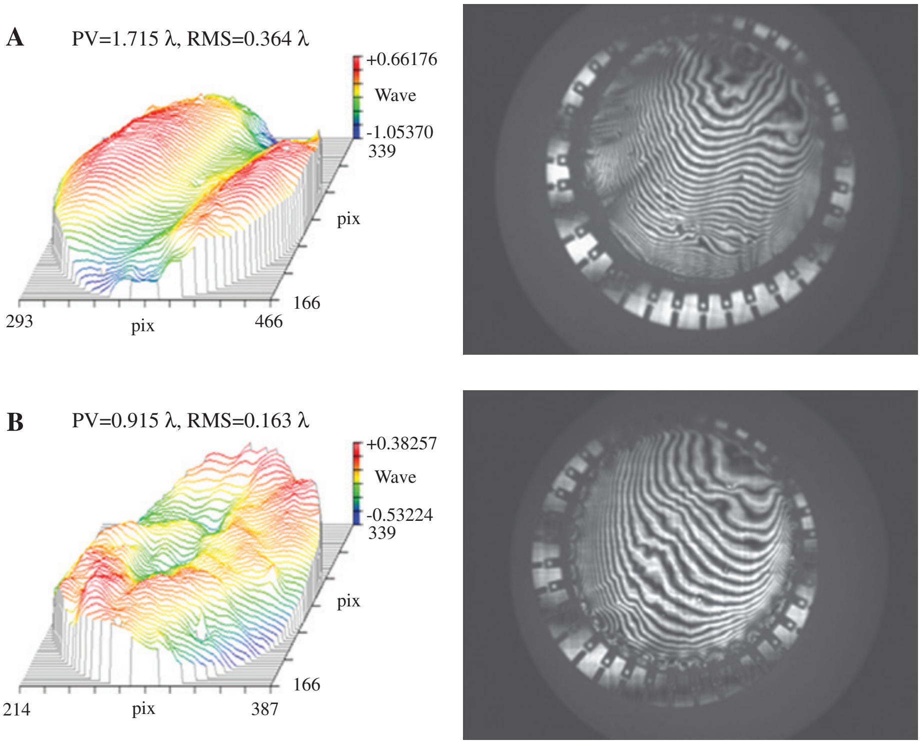


Figure 4: Optical homogeneity of (A) polyamide-imide films through direct imidization and (B) polyamide-imide films through thermal treatment suspended on a grommet.

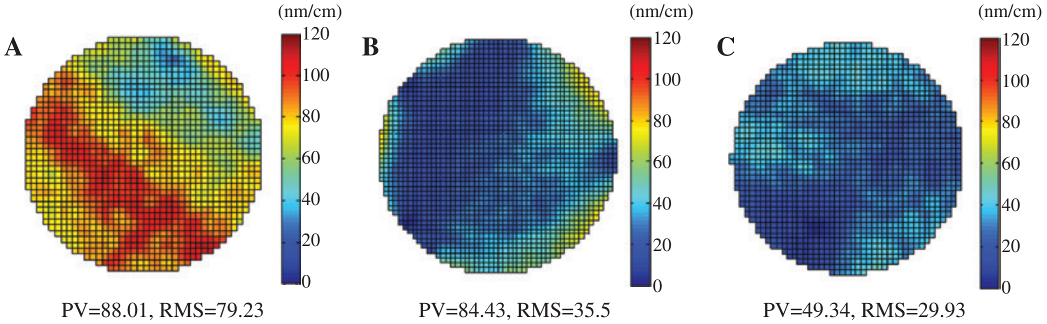


Figure 5: Stress homogeneity of commercially available Kapton film (A), and polyamide-imide films through direct imidization (B) and through thermal treatment suspended on a grommet (C).

through a high temperature annealing process by flexibly suspending the polyamide-imide membrane on a grommet.

The flexible stretching on a grommet can improve not only the optical homogeneity but also the stress homogeneity. Figure 5 shows the membrane stress homogeneity measured by Exicor AT300 birefringence measurement system. Compared with that of the commercial available Kapton PI, the stress magnitude of the prepared membrane sample is almost only half of that of Kapton in the matter of RMS, and thus is a better candidate for optical application.

4 Conclusions

In conclusion, several fluorinated polyamide-imide films were prepared from TMAC and 2,2′-bis(trifluoromethyl) benzidine through a facile *in-situ* silylation process. By incorporating fluorinated side groups, the solubility was greatly enhanced and all the chemically imidized fluorinated polyamide-imides were readily soluble in various polar solvents. Solution casting led to flexible, almost colorless polyamide-imide films with Tg of more than 300°C. Meanwhile, due to their linear chain configuration and the existence of hydrogen bonding, the polyamide-imide possess high tensile strength and high tensile modulus, and most interestingly, very low CTE of 11 ppm/°C. More importantly, the obtained polyamide-imide films showed a PV value of 0.915 λ and RMS value of 0.163 λ, which are considerably lower than those of the commercial obtained PI films. Thus, the obtained polyamide-imide films with a combination of excellent thermal-mechanical properties and excellent wavefront performance are good candidates for diffractive membrane optical application.

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