

Highly Refractive Sulfur-Containing Polyimides [1]: Molecular Design, Synthesis and Characterization

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Introduction

High refractive index (HRI) coatings with low birefringence and high transparency are urgently desired in the advanced optical areas. It has been well established that introduction of sulfur-containing moiety can effectively increase the refractive index (RI) of the polymer matrix. In the present work, a series of sulfur-containing polyimides (PIs) were designed and synthesized as shown in Scheme 1.

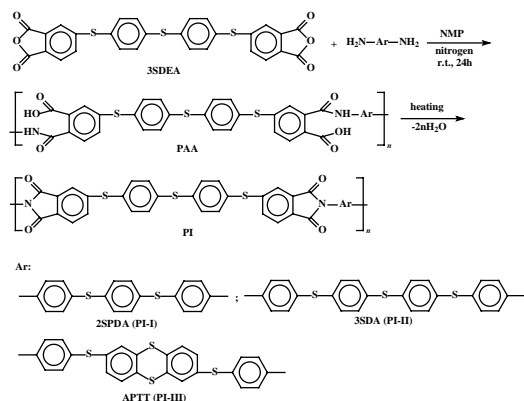
Results and Discussion

Several considerations have been addressed in the design of new HRI PIs. A Sulfur moiety is introduced to increase the RI value and a thioether linkage is used to decrease the birefringence. At the same time, the decrease of a polar imide content will improve the optical transparency of the PIs. Thus, several sulfur-containing monomers, shown in Scheme 1 were synthesized and polymerized. The thermal and optical properties of the PIs are shown in Table 1. As expected, the PIs have good thermal stabilities with the glass transition temperatures (T_g) of higher than 170°C and 5% weight loss temperatures of higher than 480°C. In addition, the PI films exhibit good transparency with the transmittance of higher than 50% at 450nm. The effects of sulfur contents of the PIs on the average refractive indices (n_{av}) measured at 632.8nm are illustrated in Figure 1. It can be seen that the n_{av} values increase with the increase of the sulfur contents of the PIs. For example, PI-III derived from the thianthrene-containing diamine APTT has the highest sulfur content (23.15%), which results in the highest n_{av} value of 1.7600. In addition, the flexible thioether linkages in the PIs endow them with the birefringences of lower than 0.01. The good combined properties make the PIs good candidates for advanced optical applications.

Table 1 Properties of PIs

PI	Diamine	S_c (%)	$[\eta]_{inh}^a$ (dL/g)	Thermal properties ^b			Optical properties ^c			
				T_g (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	λ_{cutoff} (nm)	T_{450nm} (%)	n_{av}	Δn
PI-I	2SPDA	19.3	0.66	191	492	504	424	55.8	1.7461	0.0081
PI-II	3SDA	20.5	0.62	179	489	500	400	60.3	1.7482	0.0068
PI-III	APTT	23.2	1.03	201	494	508	413	65.7	1.7600	0.0084

^a Measured with PAA solutions at a concentration of 0.5g/dL at 30°C; ^b $T_{5\%}$ and $T_{10\%}$: temperatures at 5% and 10% weight loss; ^c λ_{cutoff} : cutoff wavelength; T_{450nm} : Transmittance at 450nm; n_{av} : average refractive index measured at 632.8nm; Δn : birefringence.



Scheme 1 PI synthesis

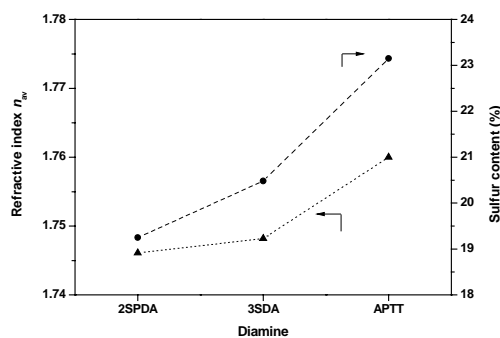


Figure 1 Refractive indices of PIs