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Synthesis and characterization of novel, soluble sulfur-containing copolyimides with high refractive indices

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Abstract High refractive index, colorless polymers with high temperature resistancy are of great industrial interest. In this study, new sulfur-containing copolyimides with high refractive indices have been synthesized via polycondensation reaction using 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA) as dianhydride monomers, and 4,4′-diaminodiphenyl sulfide (4,4′-SDA) and 2,3,5,6-tetramethyl-1,4-phenylene diamine (4MPD) as well as 3,3′-diaminodiphenyl sulfone (3,3′-DDS) as diamino monomers. The resulting copolyimides are amorphous and soluble in common organic solvents such as dimethylacetamide and *N*-methylpyrrolidone. They also exhibit very good optical properties such as high transparency (>88% at 589.6 nm) for samples with a thickness of 120–150 μm. Furthermore, higher refractive indices ranging from 1.64 to 1.72 at visible wavelengths compared to currently applied polymer materials, which show refractive indices between 1.5 and 1.6, are found. In addition, the copolyimides synthesized in this study show high thermal stability with glass transition temperatures between 273 and 306 °C.

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Introduction

In recent years, high performance polymers have become increasingly demanded in various new applications because of their exceptional thermal, mechanical, and electrical properties. Among these, polyimides, and especially aromatic polyimides, are well known for their outstanding mechanical and excellent chemical properties, like resistance to acids as well as for their heat resistance [1]. For example, this class of polymers is currently used in aerospace applications as well as high temperature resistance isolation materials [2–4].

Lately, polymers with tailored optical properties, e.g., high refractive index polymers have attracted much attention due to their potential use in advanced optoelectronic applications in the form of high performance substrates for novel display devices [5], encapsulants for organic light-emitting diodes (OLEDs), and microlens components for charge-coupled devices (CCDs) or complementary metal oxide semiconductor-contact image sensor (CMOS-CIS) [6]. Most commercially available polymers like polycarbonate (PC), poly(methyl methacrylate) (PMMA), polyethersulfone (PESU), and recently developed cyclo-olefin copolymers have refractive indices in the range of 1.48–1.58, with the exception of PESU which has a value higher than 1.6 [7].

Even the more specialized generation of high refractive index polymers, like amorphous polyetheretherketone (PEEK, n_D: 1.71, T_g: 152 °C) [8], poly(2-vinylnaphthalene) (P2VN, n_D: 1.68, T_g: 150 °C) [9], poly(*N*-vinyl-carbazole) (PVK, n_D: 1.69, T_g: 175 °C) [10], or poly(pentabromophenyl methacrylate) (PpBMA, n_D: 1.71, T_g: 37 °C) [11] tend to have different drawbacks. For example, P2VN is the only polymer which is completely colorless. PEEK, for example, exhibits a grayish color, PVK and PpBMA a yellow tone. However, the low thermal stability of these polymers is a further drawback for the above-mentioned applications.

In contrast, polyimides have an outstanding thermal stability, and their optical properties can be optimized for a variety of applications [12, 13]. A general way to improve the refractive index of a polyimide is to increase its density via the integration of large polarizable heteroatoms such as sulfur or phosphorus into the polymer chains [14–18]. However, recent studies have shown that the thioether functionality has, in fact, the strongest influence on the refractive index [19–21]. Although it was possible to reach refractive indices up to 1.70–1.76 by increasing the thioether content [22–29], the major concern remained the high charge-transfer (CT) activity of these thioethers, which was responsible for the undesirable yellowish coloration of these polymers. Another issue for most of the currently available polyimides is their insolubility in common organic solvents, which inhibits their direct processing and makes them unattractive for large-scale processing. In this case, manufacturing is only possible by processing of the polyamic acid (PAA) followed by a heat treatment for imidization.

However, it has been shown by Clair in 1986 and confirmed by Ando et al. in 1997 that sulfone groups in polyimide structures are not involved in the formation of CT complexes [30–32]. Therefore, it was assumed that sulfone-containing polyimides exhibit high refractive indices while remaining completely colorless. In this study, we report on the synthesis and characterization of amorphous copolyimides derived from 6FDA/DSDA with a 1:1 dianhydride ratio which were polymerized with several diamines such as 4MPD, 4,4′-SDA and 3,3′-DDS. The resulting copolyimides were characterized by FTIR spectroscopy, NMR spectroscopy, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). Optical properties were investigated by UV–vis spectroscopy and spectroscopic ellipsometry.

Experimental

Materials

4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, TCI Europe, >98%), 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA, TCI Europe, >96%), 4,4′-diaminodiphenyl sulfide (4,4′-SDA, TCI Europe, >98%), 2,3,5,6-tetramethyl-1,4-phenylene diamine (4MPD, Acros Organics, 99%), and 3,3′-diaminodiphenyl sulfone (3,3′-DDS, TCI Europe, >98%) were purified by sublimation. *N*,*N*-dimethylacetamide (DMAc, Acros Organics, 99%) was purified by distillation over CaH_2. Acetic anhydride (Acros Organics, >99%) and triethylamine (Acros Organics, >99%) were used as received.

General polymer synthesis

A typical synthesis route of the copolyimides is outlined in Scheme 1. A 1:1 mixture of the anhydrides 6FDA and DSDA were polymerized with three different diamines, 4,4′-SDA, 4MPD, and 3,3′-DDS, to produce the copolyimides 6FDA-4MPD/DSDA-4MPD 1:1, 6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1, and 6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1 (Fig. 1).

The preferred synthesis route of polyimides is the reaction of dianhydrides and diamines via a two-step polycondensation. Typically, PAA is first formed, followed either by chemical or thermal imidization to give the resulting polyimide. In this study, chemical imidization was exclusively used. In order to obtain high molecular weight copolyimides, side reactions and deactivation processes have to be avoided. To this end, care has been taken in using only thoroughly purified monomers and solvents. As shown in Scheme 1, PAA is obtained in a first step by adding the dianhydrides to the diamine (4,4′-SDA, 4MPD or 3,3′-DDS) in DMAc under nitrogen. After stirring the mixture for 24 h at room temperature, the resulting PAA was chemically imidized using an equimolar, 3-fold excess (based on the amount of diamine monomer) of a triethylamine/acetic anhydride mixture, which was added slowly to the viscous PAA solution. The reaction mixture was then refluxed for 30 min at 120 °C under nitrogen.

Characterization

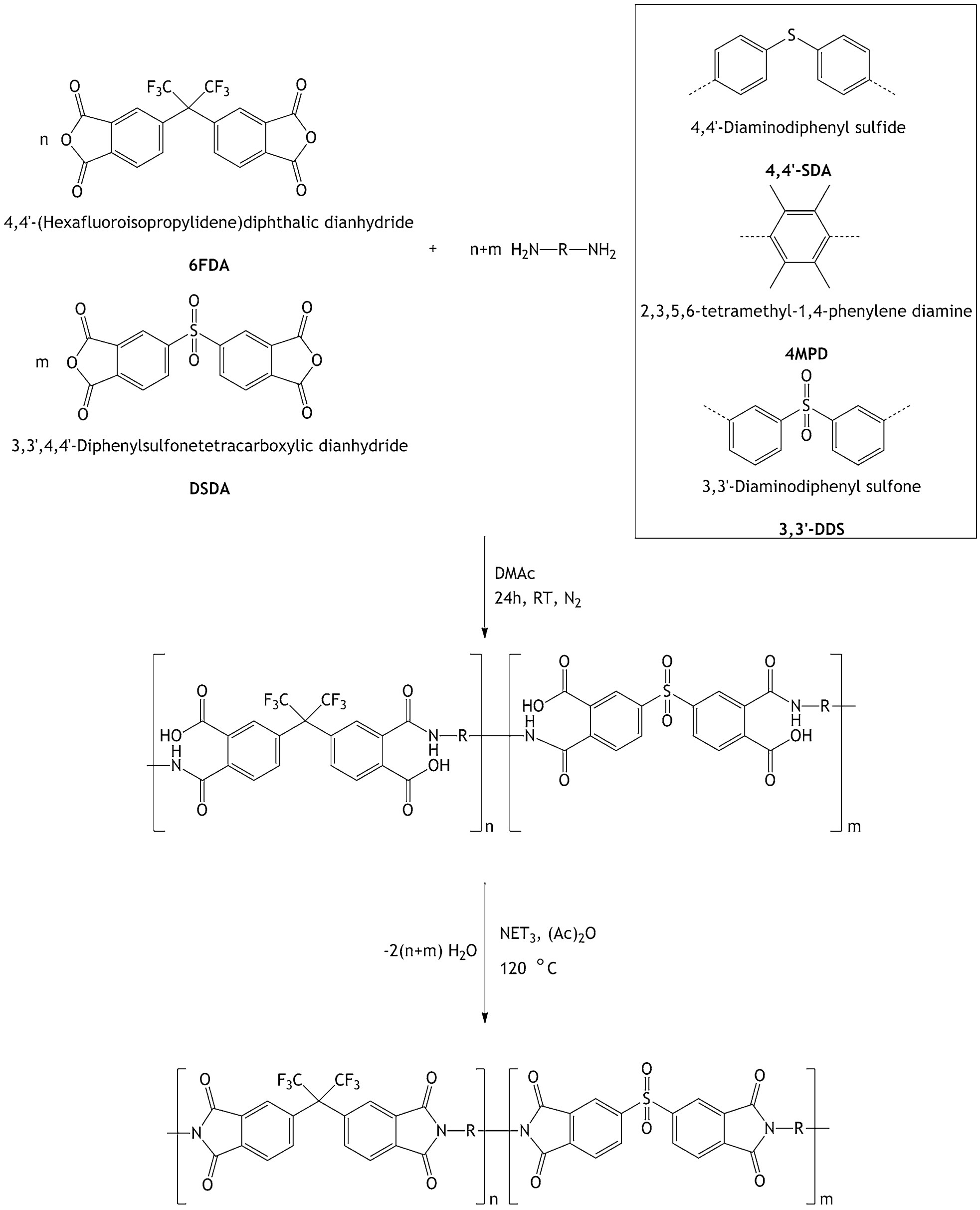
^{1}H-NMR spectra were recorded with a Bruker Avance DRX 500 spectrometer with $Si(CH_3)_4$ as internal standard at room temperature in DMSO-d_6. FTIR spectra were recorded at 4 cm^{-1} resolution with 1024 sample scans on a Nicolet 6700 equipped with an ATR unit. DSC measurements were performed on a Mettler Toledo DSC822 under nitrogen with a heating rate of 20 °C min^{-1} to a maximum of 400 °C. GPC measurements using dimethylformamide (DMF) as solvent were performed on a Viscotek VE 2001 GPC at 60 °C and a flow rate of 1.0 mL min^{-1}. UV–vis-spectrometry data were recorded on a Perkin Elmer Lambda2S with air as calibrating reference. Refractive indices were determined using a SENpro variable angle, spectroscopic ellipsometer over a spectral range covering 370–1050 nm at an incidence angle of 70°.

Synthesis of the copolyimides

6FDA-4MPD/DSDA-4MPD 1:1

4MPD (0.6570 g, 4 mmol) was placed into a moisture-free 25 mL Schlenk flask flushed with nitrogen and equipped

Scheme 1 Synthesis of the copolyimides 6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1, 6FDA-4MPD/DSDA-4MPD 1:1, and 6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1



with a neodymium stirrer. 4 mL of DMAc was added under a continuous flow of nitrogen at room temperature. Once the diamine was dissolved, a mixture of DSDA (0.7166 g, 2 mmol) and 6FDA (0.8885 g, 2 mmol) was poured in the previous solution and another 4 mL of DMAc was added. The reaction mixture was then stirred for 24 h at room temperature while maintaining a continuous flow of nitrogen. A mixture of 1.66 mL (12 mmol) triethylamine and 1.13 mL (12 mmol) acetic anhydride was then added to the previously prepared PAA solution and stirred for 10 min at room temperature. The reaction mixture was then refluxed for another 30 min under nitrogen atmosphere at 120 °C. The polyimide solution was then cooled down to room temperature and precipitated in a stirred mixture of ethanol and distilled water (1:1). The resulting polyimide threads were filtered off and washed three times with 50 mL ethanol, pulverized in a polymer mill, and washed again three times with 50 mL of ethanol. The white polymer powder was then dried in a vacuum oven for 3 days at 80 mbar and 150 °C (yield: 2.02 g; 89.3%). The peaks found in the NMR and FTIR spectra are corresponding very well with the structure of the proposed polyimide. ^{1}H-NMR (DMSO-d_6): $\delta = 2.04$ (s, 12 H, Ar–CH_3), 2.07 (s, 12 H, Ar–CH_3), 7.98 (s, 4H, Ar–*H*, *1*,*5*), 8.21–8.29 (m, 4H, Ar–*H*, *3*,*7*), 8.71–8.77 (m, 4H, Ar–*H*, *2*,*6*). FTIR (for full spectrum see Supporting Information): 1777 cm^{-1} (asymmetric C=O stretching vibration), 1718 cm^{-1} (symmetric C=O stretching vibration), 1353 cm^{-1} (C–N stretching vibration), 1141 cm^{-1} (symmetric O=S=O stretching vibration), and 730 cm^{-1} (imide five-ring deformation vibration).

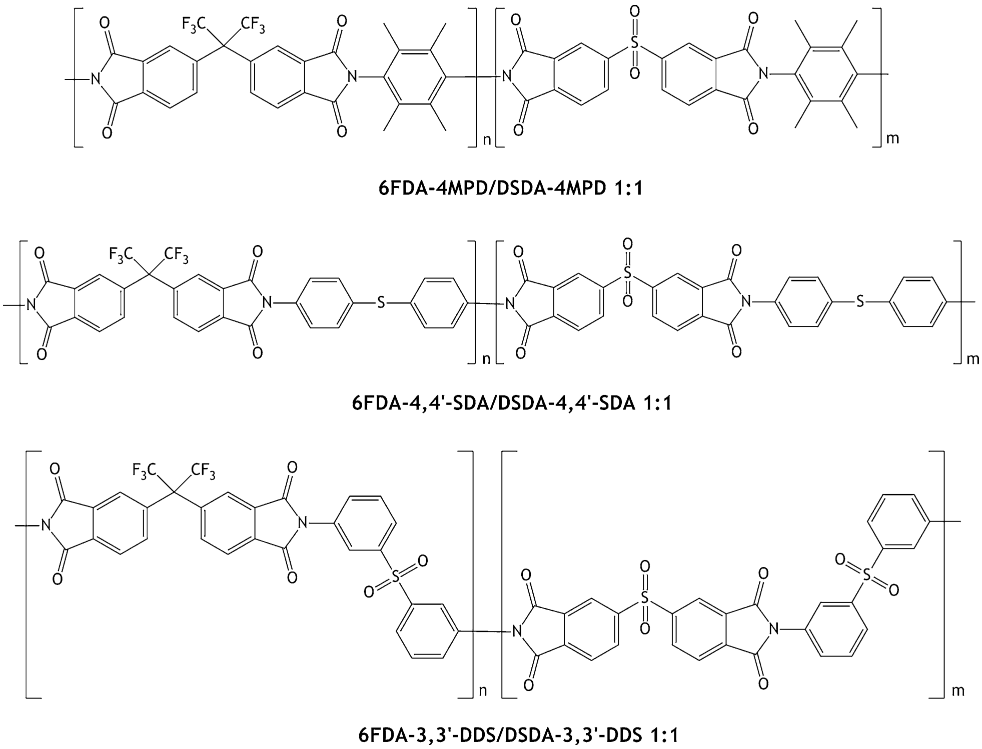


Fig. 1 Structures of the synthesized copolymers

6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1

4,4′-SDA (0.8652 g, 4 mmol) was placed into a moisture-free 25 mL Schlenk flask flushed with nitrogen and equipped with a neodymium stirrer. 4 mL of DMAc was added under a continuous flow of nitrogen at room temperature. Once the diamine was dissolved, a mixture of DSDA (0.7166 g, 2 mmol) and 6FDA (0.8885 g, 2 mmol) was poured in the previous solution and another 4 mL of DMAc was added. The reaction mixture was then stirred at room temperature for 24 h while maintaining a continuous flow of nitrogen. A mixture of 1.66 mL (12 mmol) triethylamine and 1.13 mL (12 mmol) acetic anhydride was then added to the previously prepared PAA solution and stirred for 10 min at room temperature. The reaction mixture was treated in the same way as described in the synthesis of the 6FDA-4MPD/DSDA-4MPD 1:1. Through this procedure, a pale yellow polymer powder was obtained (yield: 2.27 g, 91.8%). The peaks found in the NMR and FTIR spectra are corresponding very well with the structure of the proposed polyimide. ^{1}H-NMR (DMSO-d$_6$): $\delta = 7.48$–7.55 (m, 16H, sulfide aromatics, Ar–*H*, *4*,*5*,*9*,*10*), 7.77 (s, 2H, Ar–*H*, *1*), 7.98 (d, 2H, Ar–H, *8*), 8.19-8.22 (m, 4H, Ar–*H*, *3*,*6*), 8.63-8.68 (m, 4H, Ar–*H*, *2*,*7*). FTIR: 1777 cm^{-1} (asymmetric C=O stretching vibration), 1718 cm^{-1} (symmetric C=O stretching vibration), 1366 cm^{-1} (C–N stretching vibration), 1146 cm^{-1} (symmetric O=S=O stretching vibration), and 722 cm^{-1} (imide five-ring deformation vibration).

6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1

3,3′-DDS (0.9932 g, 4 mmol) was placed into a moisture-free 25 mL Schlenk flask flushed with nitrogen and equipped with a neodymium stirrer. 4 mL of DMAc was added under a continuous flow of nitrogen at room temperature. Once the diamine was dissolved, a mixture of DSDA (0.7166 g, 2 mmol) and 6FDA (0.8885 g, 2 mmol) was poured in the previous solution and another 4 mL of DMAc was added. The reaction mixture was treated in the same way as described in the synthesis of 6FDA-4MPD/DSDA-4MPD 1:1. Through this procedure white polymer powder was obtained (yield: 2.37 g, 91.4%). The peaks found in the NMR and FTIR spectra are corresponding very well with the structure of the proposed polyimide. ^{1}H-NMR (DMSO-d$_6$): $\delta = 7.76$ (s, 2H, Ar–*H*, *1*), 7.80–7.95 (m, 8H, sulfone aromatics, Ar–*H*, *4*,*10*), 8.00–8.06 (m, 6H, Ar–*H*, *3*,*7*,*9*), 8.16–8.22 (m, 8H, anhydride and sulfone aromatics, Ar–*H*, *2*,*5*,*8*,*11*) 8.65–8.71 (m, 4H, sulfone aromatics, Ar–*H*, *6*,*12*). FTIR: 1780 cm^{-1} (asymmetric C=O stretching vibration), 1718 cm^{-1} (symmetric C=O stretching vibration), 1366 cm^{-1} (C–N stretching vibration), 1149 cm^{-1} (symmetric O=S=O stretching vibration), and 732 cm^{-1} (imide five-ring deformation vibration).

Sample preparation for ellipsometry

For the ellipsometry measurements, a 5 wt.% solution of copolyimide in DMAc was prepared and spin-coated onto a

Si wafer. In order to get film thicknesses above 100 nm, the spin-coater was operated at a rotation speed of 1500 rpm and an acceleration of 500 rpm s^{-1} for 120 s. After spin-coating, the wafer was dried on a hot plate at 60 °C and atmospheric pressure for 2 h followed by drying in a vacuum oven at 150 °C and 80 mbar for 24 h.

Sample preparation for UV–vis spectroscopy

For UV–vis spectroscopy, free-standing film samples with thicknesses of 100 µm or more were required. Therefore, the following procedure has been applied: 300 mg of dry copolyimide powder was dissolved in 10 mL of dried DMAc and stirred with a magnetic stirrer for 3–4 h. The copolyimide solution was filtered through a syringe filter (pore size 0.45 µm), casted onto a glass mold with a diameter of 4 cm, and covered with a glass funnel capped with a tissue to prevent deposition of dust particles. The samples were heated up to 60 °C for 12 h. Free-standing film samples with an average thickness of about 120 µm were obtained. These films were stripped off from the glass mold using distilled water. Afterwards, the film samples were transferred to the vacuum oven and dried at 150 °C and 80 mbar for 2–3 days.

Results and discussion

Polymer properties

As determined by GPC, the synthesized copolyimides showed average molecular weights between 48,000 and 130,000 (see Table 1) and all of them formed highly flexible films with excellent mechanical properties. 6FDA-4MPD/DSDA-4MPD 1:1 and 6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1 have much higher molecular weights in comparison to 6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1. This is probably due to a strong −I-effect from the sulfone group of the 3,3′-DDS which slightly deactivates the amino groups and inhibits their nucleophilic properties during the formation of the PAA.

Glass transition temperatures (T_g) of the copolyimides were determined by DSC and are listed in Table 2.

Table 1 GPC data of the copolyimides detected by refractive index (RI) and UV spectroscopy (UV)

Copolyimide	M_W (g mol^{-1})	
	RI	UV
6FDA-4MPD/DSDA-4MPD 1:1	115081	116970
6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1	130253	123778
6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1	48173	47971

Table 2 DSC data of the copolyimides

Copolyimide	T_g (°C)
6FDA-4MPD/DSDA-4MPD 1:1	306
6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1	291
6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1	273

High T_g values above 270 °C were found for all polymers as expected. 6FDA-4MPD/DSDA-4MPD 1:1 has the highest T_g, probably because of the steric effect, 4MPD-induced rigidity of the polymer chains. In contrast, 6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1 and 6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1 are more flexible due to the higher number of freely rotatable single bonds in the diamine structure and have therefore lower T_g values.

The solubilities of the synthesized polyimides were tested qualitatively in common organic solvents, and the results are listed in Table 3.

The polyimides used exhibited high solubility in amidic solvents, such as DMAc, DMF, and *N*-methyl-2-pyrrolidone (NMP). Previous attempts were made by our group to synthesize the pure polyimides DSDA-4MPD, DSDA-4,4′-SDA and DSDA-3,3′-DDS via chemical imidization. Unfortunately, these attempts failed due to the insolubility of these polyimides in DMAc and NMP. Therefore, the high solubility of the copolyimides presented in this study seemed to be a result of the $-CF_3$ groups of the 6FDA which was used as a second dianhydride. Such highly soluble polymers should prove invaluable for the chemical industry when it comes to processing. Especially, spin- or dip-coating could be easily realized with those polymers.

Optical properties

UV–vis spectra of the synthesized polymers are shown in Fig. 2. Excellent transparency with transmission over 88% determined at 589.6 nm (sodium D_1-line) was observed for all the polymers (Table 4). Film thicknesses of all the measured samples were ranging between 120 and 150 µm. 6FDA-4MPD/DSDA-4MPD 1:1 and 6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1 showed cutoff wavelengths (determined at 50% transmission) below 400 nm and were, therefore, perfectly colorless. Only 6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1 had a cutoff wavelength over 400 nm and was of bright yellow color. Compared to their respective homopolymers 6FDA-4MPD (87%), 6FDA-3,3′-DDS (84%) and 6FDA-4,4′-SDA (86%) [33], slightly improved transparency was found. In comparison to commercially available polymers, transparency values are similar or slightly better than those of PC (89%) and polysulfone (84%) [7]. Only PMMA (92.5%) and the cyclo-olefin copolymers (92%) exhibit higher transparency values [7].

Table 3 Solubility of the copolyimides

Solvent	6FDA-4MPD/ DSDA-4MPD 1:1	6FDA-4,4′-SDA/ DSDA-4,4′-SDA 1:1	6FDA-3,3′-DDS/ DSDA-3,3′-DDS 1:1
Dimethylacetamide	O	O	O
Dimethylformamide	O	O	O
N-Methylpyrrolidone	O	O	O
Dimethylsulfoxide	O	O	O
Tetrahydrofurane	Δ	X	X
Acetone	Δ	X	X
Toluene	X	X	X
Cyclohexane	X	X	X
Dichloromethane	X	X	X
n-Hexane	X	X	X

The solubility was determined at 10% solid content. *O*—soluble; the solid polymer was completely dissolved in the solvent. Δ—swollen; the solid polymer was swollen by the solvent. *X*—insoluble; dissolving of the polymer <1%

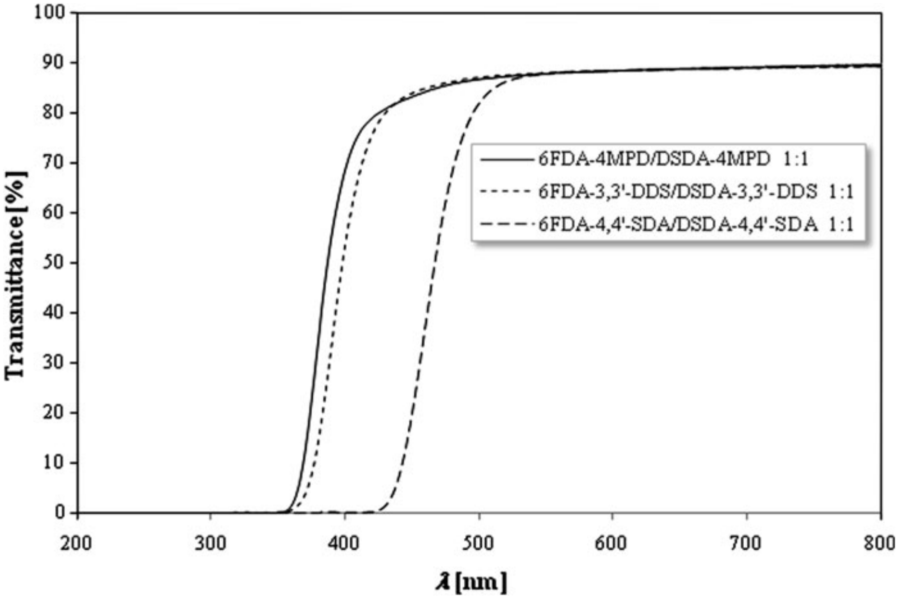


Fig. 2 Transmittance UV–vis spectra of the synthesized copolyimides (film thickness: 120–150 μm)

Table 4 Optical properties of the synthesized copolyimides

Copolyimide	Cutoff wavelength[a] (nm)	Transparency (%)	n_D[b]	V_e[c]
6FDA-4MPD/DSDA-4MPD 1:1	387	88.4	1.64	53
6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1	467	88.3	1.72	24
6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1	393	88.4	1.68	44

[a] Determined at 50% transmission; [b] Determined at 589.59 nm; [c] Abbe number

Optical dispersion curves were determined by spectroscopic ellipsometry and are displayed in Fig. 3. The ellipsometric data were fitted using either a Cauchy function for the completely transparent 6FDA-4MPD/DSDA-4MPD 1:1 and 6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1 films or a Tauc-Lorentz function for the yellowish 6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1 film.

As can be seen in Fig. 3, the copolyimides investigated in this study exhibit high refractive indices at 589.6 nm and comparably high Abbe numbers (Table 4). The Abbe number V_e used here is defined as

$$V_e = \frac{n_e - 1}{n_{F'} - n_{C'}} \tag{1}$$

where n_e, $n_{C'}$, $n_{F'}$ are the refractive indices measured at the Fraunhofer spectral lines *e* (546.07 nm), *C*′ (643.84 nm), and *F*′ (479.99 nm), respectively. For most applications, high Abbe numbers are desired because they are directly

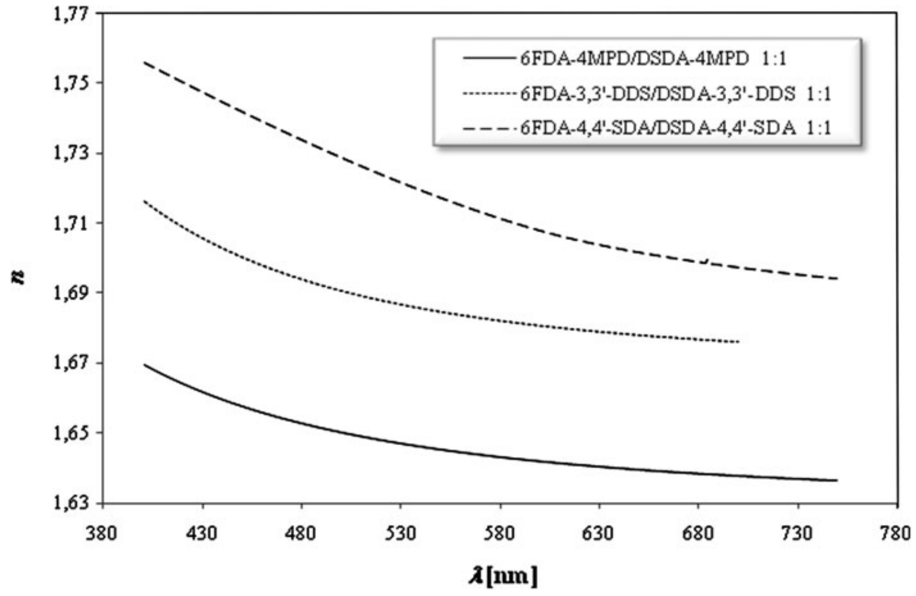


Fig. 3 Optical dispersion of the copolyimides (film thickness: 100–150 nm)

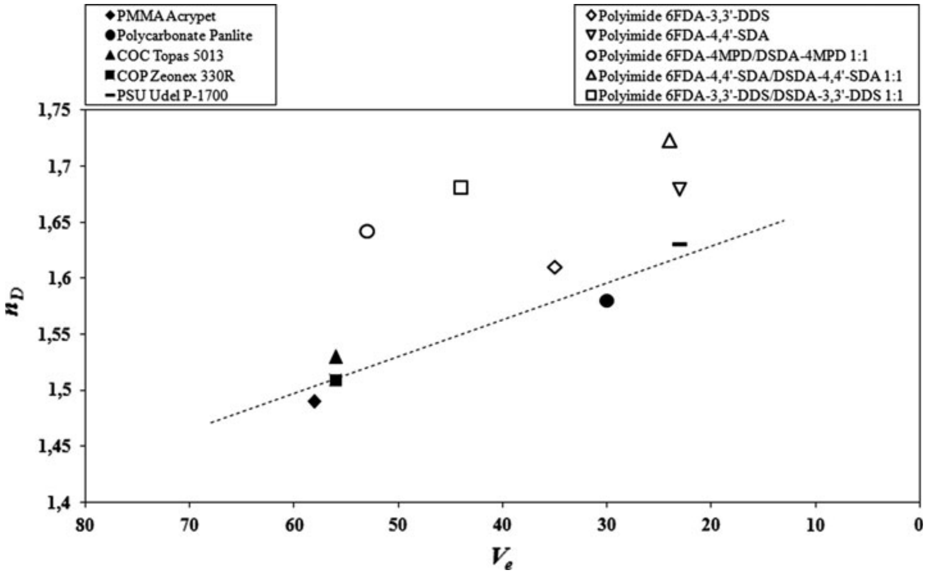


Fig. 4 Abbe diagram of synthesized copolyimides and commercially available polymers

related to low optical dispersion and low chromatic aberration. Figure 4 shows the correlation of the refractive indices and the optical dispersion in an Abbe diagram.

As can be seen in Fig. 4, the copolyimides synthesized in this study show improved refractive indices compared to the analogous homopolymers 6FDA-3,3′-DDS and 6FDA-4,4′-SDA which were also synthesized to evaluate the increase of the refractive indices. Indeed, the refractive index of 6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1 increases from 1.61 (6FDA-3,3′-DDS) to 1.68, which is an increase of 4.1%, whereas that of 6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1 increases from 1.68 (6FDA-4,4′-SDA) to 1.72, which is only an increase of 2.3%. This is probably due to the already high refractive index of 6FDA-4,4′-SDA. In fact, increasing the sulfur content in the polymer backbone is simply not as effective as for lower refractive index polymers.

As can also be seen in Fig. 4, the commercially available polymers are showing an inverse linear correlation between refractive index and Abbe number (i.e., high refractive index corresponds to low Abbe number and vice versa). The polymers synthesized in this study do not follow this correlation but rather combine low optical dispersions with high refractive indices.

Conclusion

Three novel soluble copolyimides with high refractive indices, low optical dispersions, and excellent transparencies were synthesized from commercially available dianhydrides and diamines. The thioether-containing 6FDA-4,4′-SDA/DSDA-4,4′-SDA 1:1 exhibited the highest refractive index ($n = 1.72$), but had also, like other thioether-containing polymers, a slightly yellowish color. On the other hand, the completely colorless sulfone-containing 6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1 reveals itself as the most promising polymer since it has, besides a high refractive index ($n = 1.68$), a very low optical dispersion combined with an excellent transparency (>88%) even for films up to 120 μm in thickness. 6FDA-4MPD/DSDA-4MPD 1:1 also shows high potential for optical applications with its refractive index of 1.64, which is higher than those of most commercial polymers. Furthermore, it is characterized by an even lower optical dispersion than 6FDA-3,3′-DDS/DSDA-3,3′-DDS 1:1 as well as being completely colorless. All the three polymers showed also excellent thermal properties with glass transition temperatures between 273 and 306 °C and good solubility in common organic solvents. Finally, it can be stated that sulfone groups are good substitutes for thioether groups in designing high refractive polymers while not having the disadvantage of material coloration.

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