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TiO_2-Functionalized Sulphur Containing Polyimides for Optical Applications

M. Mrsevic,* C. Staudt

Summary: Novel sulphur-containing 6FDA-SDA-DABA (4,4'-(hexafluoroisopropylidene)diphthalic anhydride – 4,4'-diaminodiphenylether – 3,5-diaminobenzoic acid) copolyimides have been synthesized to create a polymer basis for the use as optical polymers, capable of implementing TiO_2 nanoparticles by simple mixing or covalent bonding of functionalized nanoparticles. First fine dispersed nanoparticle-composites were made by simple mixing of rutile-type TiO_2 nanoparticles and the synthesized copolyimides. Moisture-absorption was measured in a climate-cabinet, transparency and cutoff wavelengths have been determined by UV-VIS spectra. The homogeneity of the composites was verified by scanning electron microscope (SEM) images of the cross sections. The polyimides show constantly low water sorption below 0.08 wt% and cutoff wavelengths below 440 nm. The implementation of nanoparticles by simple mixing was verified by SEM.

Keywords: 6FDA; nanoparticles; optics; polyimide; S-containing; water sorption

Introduction

The aim of this research is to develop new polymeric materials in order to substitute high-refractive-index-glass and ease the preparation of lenses for optical applications. The requirements for such materials are a high refractive index and Abbé-number, high transparency, low watersorption, high temperature stability and simple processing. Literature shows that sulphur or phosphorous containing polymers have very high refractive indices, also blends of polymers and TiO_2 nanoparticles show an increase of the refractive index compared to the pure polymer.[1–4] Cycloolefine copolymers show very high transparency and the lowest water sorption of the commercially available optical polymers.[5]

In this work, polyimides have been chosen as start material due to their good mechanical properties, for example high glass transition temperatures and chemical resistance, e.g. acids and protic solvents. Also commercially available polyimides show refractive indices of 1.6 to 1.7 (Matrimid 5218 and Kapton).[6,7]

The aim is to implement different features into a polyimide, which would shift the refractive index. Therefore polyimides with sulphur containing functional groups in the polymer main chain were synthesized, for example sulfide or sulfone groups. These polyimides will then be used together with TiO_2 nanoparticles, so the polyimide's refractive index should be increased by both, the sulphur content and the implemented TiO_2 nanoparticles. In order to bind the nanoparticles to the polymer material and avoid phase separation or agglomeration of the nanoparticles, the polyimides were provided with carboxyl groups, improving the attachment of the particles to the polymerchains, analogue to the usual functionalization of nanoparticles by carboxyl group carrying molecules. Also, the carboxyl groups can be used as

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Department of Organic and Macromolecular Chemistry, Heinrich-Heine-University, Universitätsstr. 1, 40225 Düsseldorf, Germany
E-mail: mrsevic@membrane-group.de

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linkage anchors for surface functionalized nanoparticles.

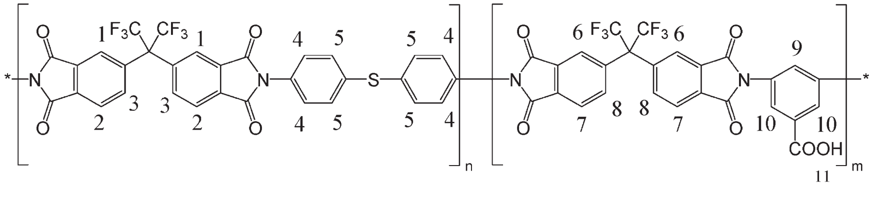
Polymer Synthesis

Copolyimides were synthesized from the dianhydride 4,4'-(hexafluoroisopropylidene)-diphthalicanhydride (6FDA) and the diamines 4,4′-diaminodiphenythioether (SDA) and Diaminobenzoic acid (DABA). SDA is used to implement thioether groups in to the polyimide, DABA carries a carboxyl group for the linkage of nanoparticles in the composites. Diamine ratios of 4:1, 9:1 and 19:1 were used for copolymerization. Figure 1 shows the structure of the synthesized polyimides.

The polyimides were obtained by synthesis of the polyamic acids in basic amide solvents like 1-Methyl-2-pyrrolidone (NMP) and N,N-Dimethylacetamide (DMAc).[8] Chemical imidisation was performed using triethyl amine and acetic anhydride as catalysts. The polyimides were then precipitated in non-solvent mixture (ethanol-water) and dried. The polyimide properties were examined by FT-IR, NMR, GPC and DSC. Since the polyaddition is severely dependent on the purities of the monomers and the solvent, high molecular masses above 20000 g · mol^{-1} can only be achieved if no impurities are in the reaction mixture. This was ensured, since all used substances were purified before usage. In order to get off the reaction solvent and the imidization substances (triethylamine and acetic anhydride) the polymer was precipitated in an ethanol-water mixture. Additional washing of the polymer powder with ethanol removed the remaining water. The drying of the polymer in vacuum (80 mbar) at 150 °C for one week finally eliminated the remaining traces of ethanol. It can be assumed that the resulting polymer powder is absolutely pure, since no traces of solvent or other used substances can be seen neither in the IR nor the NMR spectra. The diamine ratios in the copolymers could be verified by the NMR spectra. The ratios between the proton integrals of single protons of DABA and SDA show the same ratio as the initial mass of the diamine monomers for the synthesis (Figure 2).

GPC and DSC measurements were made to obtain basic polymer properties of the synthesized polyimides. All polyimides show glass transition temperatures (T_g) between 286 and 299 °C. The T_g of the DABA containing polymers is slightly higher than these of the 6FDA-SDA polymer. Also, the T_g increases with the DABA content, whereas the TiO_2-containing polyimide shows a lower T_g than the pure polyimide. (Table 1). The polymers show average molecular masses of up to 134000 g · mol^{-1}.

In a first step polymer-TiO_2 nanoparticle blends were made by solving the polyimides and TiO_2 nanoparticles (rutile-type, 20 × 50 nm) in THF. The polymer – TiO_2 mass ratio was 10:1, the THF solution contained 3.3 mass% polymer solid. The suspension was filtered and casted on metal plates to obtain transparent films after evaporation of the solvent. After evaporation, the nanocomposites were dried at 80 mbar vacuum and 150 °C to remove all solvent residues from the films. Therefore it can be assumed, that the nanocomposites



n : m = 4:1, 9:1, 19:1, 1:0

Figure 1.
General structure of the synthesized copolyimides of 6FDA-SDA-DABA.

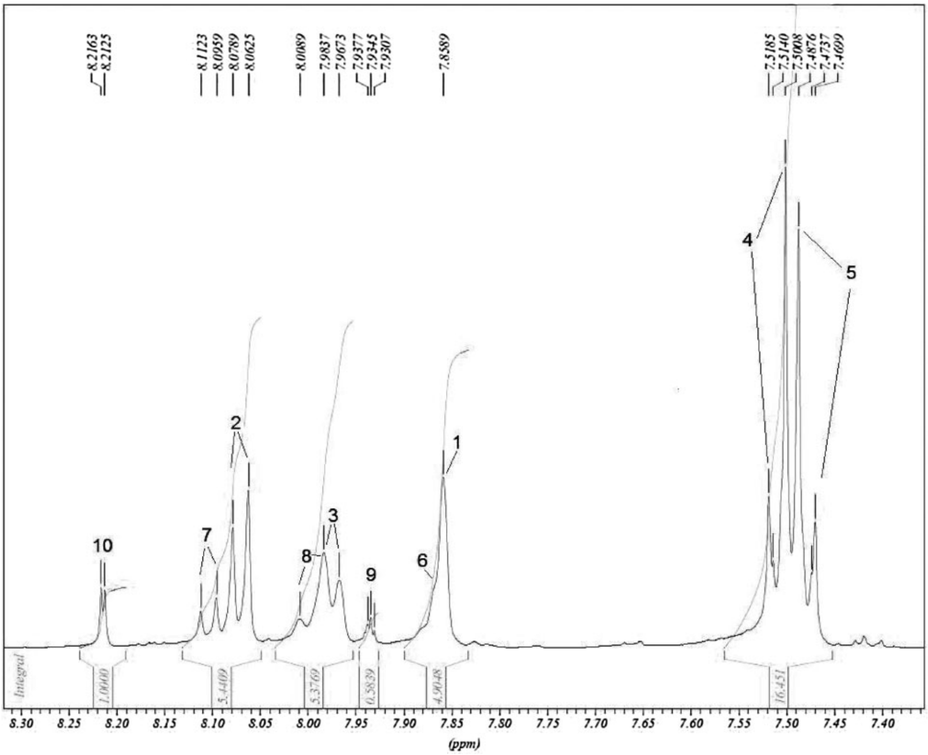


Figure 2.
^{1}H-NMR spectrum of a 6FDA-SDA-DABA 4:1 copolyimide. Peak No. 10 is equivalent to the two aromatic protons in in ortho-position to the carboxyl group of the DABA. Peaks No. 4 and 5 are equivalent to the eight aromatic protons on the SDA. The integral ratio of these two peaks (16 to 1) is equivalent to the monomer ratio of 4:1 in the polymer. See Figure 1 for the characterization of the other peaks.

consist of nothing but the nanoparticles and the pure polyimide powder. Polymers with and without DABA content were used for the composites. The implementation of nanoparticles was examined by cross section SEM images of the casted films (Figure 3). These show that the implementation of nanoparticles by simple mixing/solving only works with the DABA copolymerized polyimides. The image of the 6FDA-SDA-DABA 19:1 film shows dispersed nanoparticles in the size of the used TiO_2-powder. No agglomeration was observed in the composite-films. TiO_2 nanoparticles that agglomerated due to moisture absorption before mixing with the polymer were also built into the DABA-copolymers. Figure 4 shows nanoparticle agglomerates in bulk before mixing and dispersed in the 6FDA-SDA-DABA 4:1 in the average size of 100 nm.

Table 1.
Glass transition temperatures of the polyimides.

Polyimide type	1^{st} heating$^{a)}$	2^{nd} heating$^{b)}$
	T_g	T_g
	°C	°C
6FDA-SDA	288	301
6FDA-SDA-DABA 19:1	286	301
6FDA-SDA-DABA 9:1	289	305
6FDA-SDA-DABA 4:1	299	311
6FDA-SDA-DABA 9:1 TiO_2	280	300

$^{a)}$ramp: 20–350 °C; heating rate: 15 K/min
$^{b)}$ramp: 20–450 °C; heating rate: 15 K/min

Measurements

UV-VIS Spectra in Figure 5 show the transparency of the polyimide films and its

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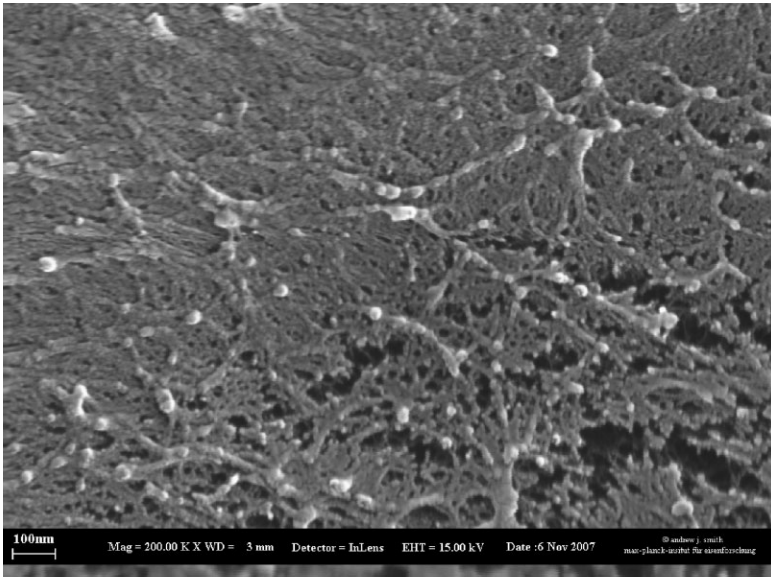

Figure 3.
Cross section SEM image of a 6FDA-SDA-DABA 19:1 – TiO_2 nanoparticle composite.

dependency of the DABA content and the presence of TiO_2 nanoparticles. The spectra show, that there is a slight influence of the DABA content on the cutoff wavelength, but not on the transparency. The same effect can be observed on the TiO_2-modified sample. It shifts the cutoff wavelength of the 6FDA-SDA-DABA 19:1 from 446 nm to 420 nm. The cutoff wavelengths vary between 417 and 443 nm (50% transparency). The measured transparencies are mainly affected by the film casting process. Best results were achieved by coating a 10 wt% THF solution with an applicator. Nevertheless higher transparencies should be achieved by optimized film casting.

Water sorption measurements were performed using a climate cabinet. Polyimide samples were dried two weeks at 150 °C and 30 mbar to evaporate solvent residues and moisture until mass constancy. Then the samples were weighed and then stored at 50 °C and 98% moisture in the climate cabinet for 10 days, weighing the samples every day to determine the water uptake. Polyimides with different DABA

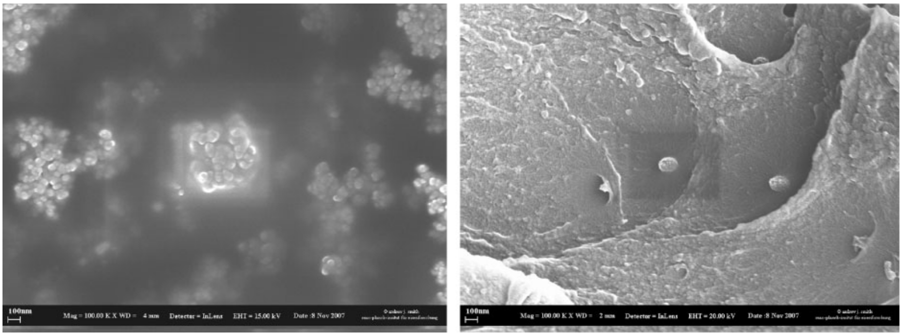

Figure 4.
TiO_2 nanoparticles that absorbed moisture during storage before and after implementation in a 6FDA-SDA-DABA 4:1 copolymer.

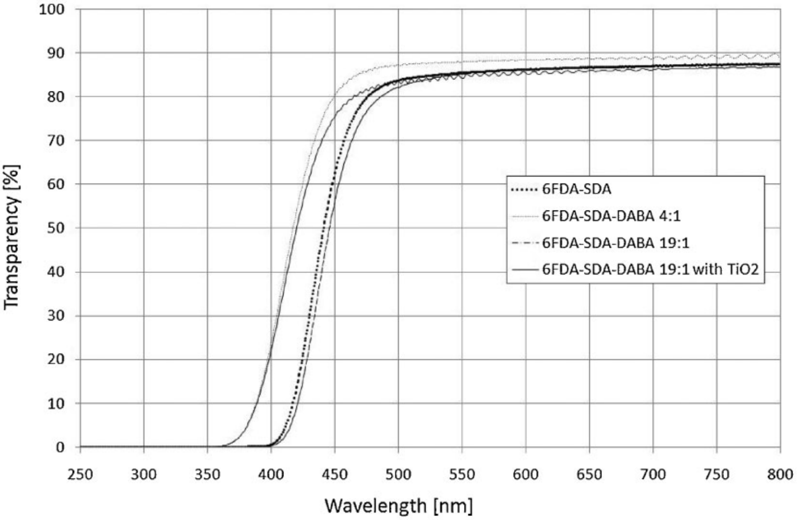

Figure 5.
UV-VIS spectra of the synthesized polyimides. Comparison between DABA-copolyimides and TiO_2-containing composites.

content and samples with TiO_2 nanoparticles were tested, to prove the effect of the implemented polar carboxyl group and of the nanoparticles as well. All samples had in common that the highest water uptake was measured after the first day of treatment. In the following days the masss of the polymers decreased to the values before treatment. The DABA content seems not to have any effect in the measured concentration. All polyimides showed a water uptake of 0.03 to 0.08 mass % after the first day of treatment. TiO_2-modified polyimides show water uptakes of 0.16 to 0.25 mass % after the first day but a rapid decrease to zero uptake after 4 days of treatment was found. Table 2 gives an overview of the water sorption measurements.

Table 2.
water sorption of the polyimides.

Polyimide type	water uptake[a) 24 h]	water uptake[a) 7 days]
	mass %	mass %
6FDA-SDA	0.08	0
6FDA-SDA-DABA 19:1	0.06	0.01
6FDA-SDA-DABA 9:1	0.03	0.01
6FDA-SDA-DABA 4:1	0.04	0
6FDA-SDA-DABA 9:1 TiO_2	0,25	0,01
6FDA-SDA-DABA 4:1 TiO_2	0,16	0,01

a)climate cabinet: 50 °C, 98% moisture

Experimental Part

Materials used for syntheses and sample preparation: 1-methyl-2-pyrrolidone (GC >99,5%) and N,N-dimethylacetamide (>99%, for synthesis) were obtained from Merck. Both solvents were refluxed in minimum eight hours over calcium hydride for desiccation before distillation. The first fraction of the distillate was discarded. 4,4'-diaminodiphenylsulfide (4,4'-SDA, Sigma Aldrich) has been purified by sublimation at 0,1 mbar and 190 °C. 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, Alfa Aesar) has been purified by sublimation at 0,1 mbar and 215 °C. 3,5-diaminobenzoic acid (DABA, Merck) has been purified by sublimation at 0,1 mbar and 195 °C. Acetic anhydride (J.T. Baker, 97%), triethylamine (Acros organics, 99%) for the imidization and tetrahydrofuran (Prolabo, 99,5%) for film casting were used as received.

TiO_2-nanopowder was purchased from Sigma-Aldrich (purity >99,5%) and used as received.

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Sample preparation: The samples that were used for UV-VIS measurements, SEM micrographs and water sorption measurements were prepared as followed: 300 mg polymer powder was dissolved in 10 ml THF and casted on a metal plate with a diameter of 6 cm. The solvent was evaporated at room temperature overnight, leaving a 120 μm thick polymer film. After drying at 150 °C and 80 mbar vacuum the polymer films were used for transmission measurements in the wavelength range of 250–800 nm as well as for the cross-section SEM micrographs. Also, the same sample preparation method was used for the water sorption experiments. Therefore 450 mg polymer was dissolved in 10 ml THF to achieve higher sample weights.

^{1}H-NMR spectra have been measured on a Bruker Avance DRX 500 MHz spectrometer, using THF-d_8 as solvent. DSC measurements have been made on a Mettler Toledo DSC 822e. The samples were heated three times from 20 to 200 °C and cooled to 20 °C again. Then the samples were heated up to 350 °C, cooled down to 20 °C and heated up again to 450 °C to determine the glass transition temperatures. UV-VIS measurements were made on a Perkin Elmer Lambda2S spectrometer using 120 μm thick polymer and nanocomposite films. Water sorption experiments have been done with a Weiss Umwelttechnik WK1 - 180/80 climate cabinet, measuring at 50 °C and 98% relative humidity. Three samples of each polymer type or nanocomposite type have been measured simultaneously to give an average of the amount of the water that was absorbed by the samples. The average weight of each sample was 450 mg. SEM micrographs were made on the Max Planck Institut für Eisenforschung GmbH from cross-sections of broken polyimide films. Therefore a LEO 1550VP Field Emission SEM -Instrument in inlens mode was used. The sample distance was 8 mm, using an accelerating voltage between 5 and 15 kV. Samples without nanoparticles had to be sputtered with gold for 15 seconds before measuring. The nanocomposites and the pure TiO_2 nanopowder could be measured without sputtering due to the semiconducting ability of the TiO_2.

Conclusion

Several new sulphur-containing copolyimides have been synthesized and analyzed in terms of their structure, transparency and water sorption. The polyimides show constant high glass transition temperatures from 286 to 299 °C and water sorption below 0.08 wt%. Transparencies of up to 88% and cutoff wavelengths of 417 nm have been measured via UV-VIS spectra. All copolyimides synthesized obtain carboxyl groups, which can be used to bind functionalized nanoparticles as well as they allow the creation of polyimide-nanoparticle composites by simple mixing of the materials. First TiO_2 nanoparticle composites were made and compared with the samples without nanoparticles. The Tg of those composites is lowered by 9 K and slight reduction of the cutoff wavelength in the UV-VIS spectra is observed, compared to the origin copolyimide. The homogenous insertion of the nanoparticles was verified by SEM images. In the future, refractive index measurements via ellipsometry will be performed, also dianhydrides which should enable higher refractive indices, than the 6FDA will be used for the polyimide synthesis. To enable higher concentrations of the nanoparticles in the composites, the binding of functionalized nanoparticles on the carboxyl groups will be investigated.

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