 DOI: 10.1002/masy.201100052

Synthesis and Characterization of Polyetherimides with 3-Methoxy-1,2-propanediol Moieties

Maik Lange,[1,2] *Karola Luetzow,*[1] *Axel T. Neffe,*[1,2] *Andreas Lendlein**[1,2]

Summary: Polyetherimides have been evaluated as non-toxic and steam-sterilizable and are therefore potentially suited for biomedical applications. To enable a broader range of potential applications, polyetherimides with lower T_g, higher elasticity at room temperature and better processability are required. Our concept was to explore, whether the incorporation of 3-methoxy-1,2-propanediol moieties in the main chain lead to a reduction of T_g and increase the elastic properties of the polymer compared to commercially available polyetherimides from 4,4′-(4,4′-isopropylidenediphenoxy)-bis(phthalic anhydride) and 1,3-diaminobenzene. Two different monomers were synthesized and co-condensated with each other or using 4,4′-(4,4′-isopropylidene-diphenoxy)bis(phthalic anhydride), respectively. The results proofed the successful synthesis and polymerization leading to polymers with molecular weights up to $M_n = 6{,}400$ g/mol. The polymers showed lowered T_g, resistance to heat up to 400 °C, tendencies to reduced contact angles and partially reduced E-moduli in comparison to the commercial polyetherimide ULTEM 1000.

Keywords: biomaterials; glass transition temperature; MALDI MS; mechanical properties; polyimides

Introduction

Biomaterials have to fulfil the complex requirements of biomedical applications.[1] Therefore, polymer systems with adjustable properties are of high significance.[2–5] The starting point of this work is a commercially available polymer, whose structural design forms the basis for building a polymer system, whose properties can be tailored systematically. Polyetherimides (PEI) often exhibit stability to various solvents, mechanical stability and temperature tolerances above 200 °C, so that they are steam sterilizable. Sterilization by steam is considered beneficial because it is easy to perform and does not require use of toxic substances or γ-irradiation.[6–7] Additionally to this, biological analyses revealed that many PEIs are non-toxic.[8–10] However, as they consist of aromatic moieties the surfaces of the most PEIs are highly hydrophobic. At ambient temperature PEIs are glassy and amorphous polymers exhibiting high stiffness.[11] As many potential applications require a certain flexibility of the material, the mechanical properties of the established PEIs are limiting their applicability.

Here, we aimed at reducing the T_g of PEIs to adjust its elastic properties. For this purpose, we aimed at including moieties into the main chain, which increase the main chain flexibility and would have small dangling side chains to reduce T_g. PEI synthesis is performed by condensating diamines with diphthalic anhydride. 1,3-diaminobenzene and 4,4′-(4,4′-isopropylidenephenoxy)-bis-(phthalicanhydride) are comonomers which are commonly applied in the commercially available PEIs. For creating a PEI based polymer system with

[1] Center for Biomaterial Development and Berlin-Brandenburg Center for Regenerative Therapies, Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, Kantstrasse 55, 14513 Teltow, Germany
Fax: +49-3328-352452;
E-mail: andreas.lendlein@hzg.de
[2] Institute of Chemistry, University of Potsdam, 14476 Potsdam, Germany

adjustable mechanical properties, two monomers, a diamine and a diphthalic anhydride, were designed and prepared. 3-Methoxy-1,2-propanediol was chosen because of its low melting point and as diol can replace bisphenol A in a synthetic route analogous to the procedures described in the literature for other polyetherimides. The methoxy side chain was thought to reduce the formation of interchain interactions between neighboured polymer chains by introducing sterical hindrances. Therefore an additional reduction in the T_g of the final PEI was expected. In the following, the synthesis and characterization of the new monomers and polymers is described.

Materials and Methods

Materials

1-Fluoro-4-nitrobenzene (97%) (***1***), 4-Nitrophthalonitrile (99%) (***5***) and 4,4′-(4,4′-isopropylidenephenoxy)-bis-(phthalicanhydride) (97%) (***9***) were purchased from Sigma-Aldrich GmbH (Germany). 3-Methoxy-1,2-propanediol (98%) (***2***) was purchased from ABCR GmbH & Co. KG (Germany). The comparing standard polyetherimide synthesized from 4,4′-(4,4′-isopropylidenephenoxy)-bis-(phthalicanhydride) and 1,3-diaminobenzene (Ultem® 1000) was purchased from GE Plastics (USA). All further used solvents and chemicals were purchased from Sigma-Aldrich GmbH (Germany) and Merck KGaA (Germany) and used as received, unless mentioned in the text.

Analytical Methods

NMR spectra (^{1}H, ^{13}C) were recorded at room temperature with a Bruker Avance 500 spectrometer. Relaxation times were set to 15 s in ^{1}H-NMR to enable correct integration of the signals.

Differential scanning calorimetry (DSC) measurements were conducted with a Netzsch DSC 204 (heating rate 10 K · min^{-1}, −100 °C to 300 °C for monomers, 0 °C to 300 °C for oligomers). Measuring was carried out in dynamic measuring mode under a nitrogen atmosphere (heated from 20 °C to 300 °C, cooled and reheated to 300 °C).

TGA (Netzsch TG 209) was measured from 25 °C to 600 °C under nitrogen atmosphere using a heating rate of 10 °C per minute.

Mass spectra were obtained in positive ion mode using an integrated ESI-Q-TOF$_{micro}$ quadruple time-of-flight mass spectrometer (Micromass, Manchester, UK) equipped with an ESI source. The MALDI-TOF spectrum of ***11*** was measured using a MALDI-TOF/TOF (Ultraflextreme MALDI-TOF/TOF, Bruker Daltonics).

Molecular weights of all polymers were determined using multidetector GPC (RI-detector (Shodex), light scattering and viscosity detector (Viscotek). GPC was conducted in chloroform using 0.2% toluene as internal standard and a polymer concentration of 2mg/mL. M_n was assessed based on a universal calibration.

Contact angles were measured using the captive bubble method (DSA 100, Krüss, Software DSA 1.90.0.14, water-air system, $n = 2$) on three different surface areas per sample resulting in $n = 30$ values for advancing (Θ_{adv}) and receding (Θ_{rec}) contact angle, as well as hysteresis.

Tensile tests (Zwick 2.5, force sensor 200 N, testXpert Software Version 11.02, $n = 5$) were performed for all samples at room temperature and elongation of 2 mm per minute.

Monomer Synthesis

1,1′-[(3-Methoxypropane-1,2-diyl)bis(oxy)]-bis(4-nitrobenzene) ***3***

The dinitrocompound 1,1′-[(3-methoxypropane-1,2-diyl)bis(oxy)]bis(4-nitrobenzene) ***3*** was synthesized by mixing 27.5 g of 3-methoxy-1,2-propanediol (0.264 mol, 1 equiv.), 82 g 1-Fluoro-4-nitrobenzene (0.581 mol, 2.2 equiv.) and 38.5 g K_2CO_3 (0.278 mol, 1.05 equiv.) in dry 1:1 v/v toluene/*N,N*-dimethylformamide (600 mL) under nitrogen atmosphere in a 1 L three-necked round bottom flask equipped with a Dean-Stark apparatus and stirring under reflux at 140 °C for 72 h. Finally, the toluene was

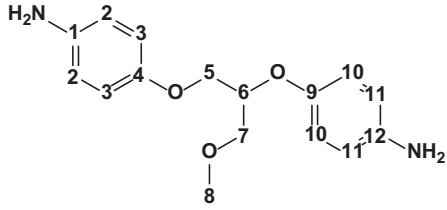
removed under reduced pressure and the brown solution was precipitated in water to give a yellow precipitate (71.2 g crude product, yield 77%). To purify the crude product, re-precipitation from ethanol solution in water was performed three times to give a white powder (65.9 g).

Yield 72%; mp 94 °C; ^{1}H-NMR (500 MHz, DMSO-d_6), $\delta = 8.19$ (mc, 4H $_{aromatic}$); 7.26 (mc, 2H $_{aromatic}$); 7.15 (mc, 2H $_{aromatic}$); 5.17 (mc, 1H); 4.43 (mc, 2H); 3.74 (mc, 2H); 3.32 (s, 3H) ppm; elemental analysis: calculated ($C_{16}H_{16}N_2O_7$): C 55.17%, H 4.63%, N 8.04%; found: C 55.37%, H 4.92%, N 8.01%; mass spectrometry: calculated 348.0958 g/mol, found 348.0969 g/mol.

*4,4′-[(3-Methoxypropane-1,2-diyl)bis(oxy)]-dianiline **4***

In a 500 ml round bottom flask equipped with thermometer, dropping funnel and reflux condenser, 30 g of ***3*** (86 mmol) and 0.5 g Pd/C were mixed with 300 ml pure ethanol and heated up to reflux. Hydrazine solution (36% solution in water, 50 g, 1.55 mol) was added drop wise (48 h) until the TLC (Silica gel, $CHCl_3$, compound ***3*** is not migrating ($R_f = 0$)) showed no further residues of compound ***3***. The brown solution was cooled to room temperature, Pd/C filtered off using a syringe filter and extracted with 3×50 ml chloroform to remove unreacted residues of compound ***3***. After removing the solvents and drying in vacuum a solid white powder was obtained (23.6 g).

Yield 95%, mp 76 °C, ^{1}H-NMR (500 MHz, DMF-d_7) $\delta = 6.79$ (mc, 2H $_{aromatic}$), 6.72 (mc, 2H $_{aromatic}$), 6.63 (mc, 4H $_{aromatic}$), 4.71 (s, broad, 4H), 4.44 (mc, 1H), 4.05 (mc, 2H), 3.65 (mc, 2H), 3.34 (s, 3H) ppm; ^{13}C-NMR (125 MHz, DMF-d_7) $\delta = 150.5$ & 149.6 (C4, C 9), 143.8 & 143.2 (C1, C12), 118.2/115.7/115.2/115.1 (C2, C3, C10, C11), 77.6 (C6), 71.6 (C7), 68.2 (C5), 58.6 (C8) ppm; elemental analysis: calculated ($C_{16}H_{20}N_2O_3$): C 66.65%, H 6.99%, N 9.72%; found: C 66.65%, H 7.24%, N 9.74%; mass spectrometry: calculated 288.1480 g/mol, found 288.1474 g/mol.



4

*4,4′-[(3-Methoxypropane-1,2-diyl)bis(oxy)]-dibenzene-1,2-dicarbonitrile **6***

In a dry three-necked round bottom flask equipped with dropping funnel, drying tube and thermometer, 4-fluorophthalonitril (99.5 g, 0.574 mol) and potassium carbonate (40.2 g, 0.291 mol) were dissolved/suspended in dry DMSO (300 mL) at room temperature. 3-Methoxy-1,2-propanediol (27.4 g, 0.261 mol) was added dropwise using a dropping funnel. The solution was stirred for 48 h and afterwards precipitated in water. Re-precipitation from ethanol in water gave 68 g of grey powder.

Yield 73%, mp 155 °C, ^{1}H-NMR (500 MHz, DMSO-d_6) $\delta = 8.03$ (mc, 1H $_{aromatic}$), 7.86 (mc, 1H $_{aromatic}$), 7.78 (mc, 1H $_{aromatic}$), 7.53 (mc, 1H $_{aromatic}$), 7.44 (mc, 1H $_{aromatic}$), 5.24 (mc, 1H), 4.45 (mc, 2H), 3.71 (mc, 2H), 3.29 (s, 3H) ppm; elemental analysis: calculated ($C_{20}H_{14}N_4O_3$): C 67.03%, H 3.94%, N 15.63%; found: C 64.89%, H 3.67%, N 16.89%; mass spectrometry: calculated 358.1055 g/mol, found 358.1066 g/mol.

*4,4′-[(3-Methoxypropane-1,2-diyl)bis(oxy)]-dibenzene-1,2-dicarboxylic acid **7***

In a two-necked round bottom flask with reflux condenser and thermometer, the nitrile compound ***6*** (15.5 g, 43 mmol) and potassium hydroxide (18.6 g, 0.331 mol) were dissolved/suspended in 1:1 v/v ethanol/water and heated up to reflux. The reaction was stirred until no further development of ammonia was detected and the suspension became a solution. Ethanol was removed, the aqueous solution acidified with HCl to $pH = 1$ and extracted with diethyl ether. The aqueous solution was completely concentrated and the salty solid

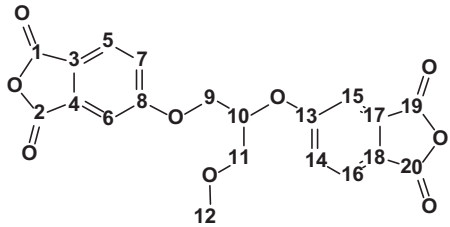
extracted with ethanol to remove the KCl. Finally, the ethanol was removed and the brown solid (16.5 g) dried in vacuum (2 d, 10^{-6} mbar).

Yield 87%, ^{1}H-NMR (500 MHz, DMSO-d_6) $\delta = 12.9$ (broad s, H of acid), 7.73 (mc, 2H $_{aromatic}$), 7.18 (mc, 2H $_{aromatic}$), 7.09 (mc, 2H $_{aromatic}$), 5.04 (mc, 1H), 4.34 (mc, 2H), 3.70 (mc, 2H), 3.31 (s, 3H) ppm; elemental analysis: calculated ($C_{20}H_{18}O_{11}$): C 55.30%, H 4.18%; found: C 54.65%, H 4.39%; mass spectrometry: calculated 435.0950 g/mol, found 435.0927 g/mol.

4,4′-[(3-Methoxypropane-1,2-diyl)bis(oxy)]-bis(phthalic anhydride) ***8***

In a dry three-necked round bottom flask equipped with thermometer, reflux condenser, drying tube and nitrogen purge, 10 g (22.9 mmol) ***8*** was dissolved in 1:1 v/v pure acetic acid/acetic anhydride. The amber solution was heated for reflux for 48 h and the acetic acid distilled off afterwards. The black solution was stored in the freezer (−18 °C) for 2 weeks until a grey precipitate could be filtered off. The precipitate was dried in vacuum (5 d, 10^{-6} mbar) and used as received.

Yield: n.d.; ^{1}H-NMR (500 MHz, DMF-d_7) $\delta = 8.03$ (mc, 2H $_{aromatic}$), 7.83 (as, 1H $_{aromatic}$), 7.67 (mc, 2H $_{aromatic}$), 7.56 (mc, 1H $_{aromatic}$), 5.46 (s, 1H), 4.70 (mc, 2H), 3.89 (mc, 2H), 3.40 (s, 3H) ppm; ^{13}C-NMR (125 MHz, DMF-d_7) $\delta = 167.2$ & 165.5 (C1, C2, C19, C 20), 158.4 & 158.1 (C8, C13), 135.1 (C4, C17), 129.4 & 129.3 (C6, C15), 121.7 & 121.6 (C3, C18), 114.5/113.3/113.2/111.9 (C5, C7, C14, C16), 73.6 (C11), 68.7 (C 9), 65.6 (C10), 56.4 (C12) ppm; mass spectrometry: calculated 398.0638 g/mol, found 398.0624 g/mol.



8

Polymer Synthesis

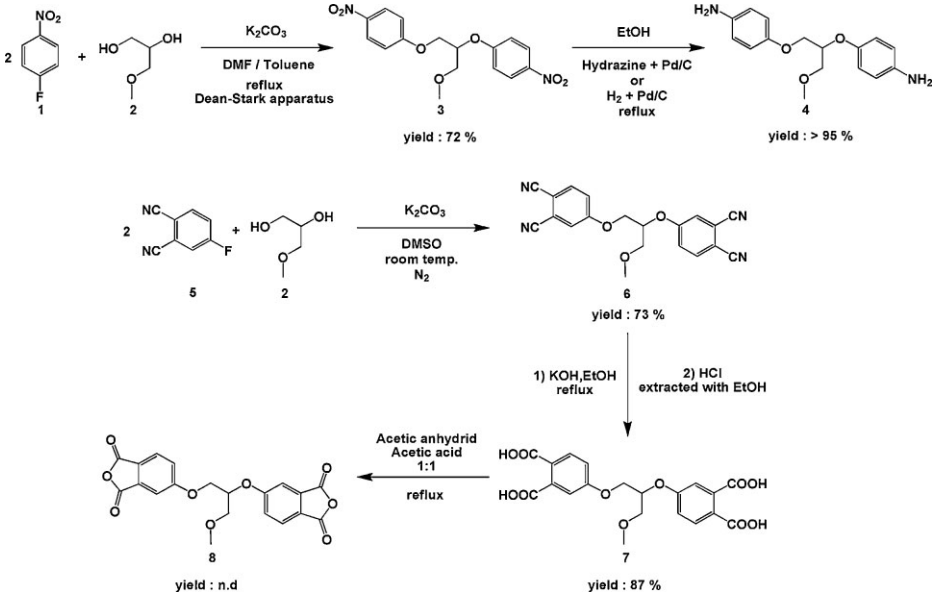
In a dried three-necked round bottom flask equipped with thermometer, dropping funnel, drying tube and reflux condenser, the phthalic andydride (1.01 equivalent) (***8*** or ***9***) was dissolved in dry *N,N*-dimethylacetamide (2 mL DMAc per g anhydride). The solution was heated to 60 °C and the diamine ***4*** (1.0 mol per 1.01 mol phthalic anhydride) dissolved in DMAc (2 mL per g diamine) was added drop wise to the stirred solution. After 2 h of reaction the solution became viscous and 20 mL (1:1 v/v) acetic anhydride/dry pyridine was added and further reacted for 24 h at 60 °C. The polymer was precipitated in methanol, dissolved in DMAc and re-precipitated in methanol again and finally dried for 2 d (10^{-6} mbar). To determine the molecular weights GPC ($CHCl_3$) was performed. In the case of the polymer ***11***, which was synthesized by co-condensation of both new synthesised monomers, a MALDI-TOF (Ultraflexetreme MALDI-TOF/TOF, Bruker Daltonics) mass spectrum was measured. For tensile tests and contact angle measurements polymeric films from 20 wt.% in CH_2Cl_2 were cast on a glass plate using a coating knife (0.4 μm) and dried in vacuum (24 h, 60 °C, 10 mbar and finally 48 h, RT, 10^{-6} mbar).

Results and Discussion

Synthesis of the Monomers

Synthesis of the monomers (Scheme 1) was adopted from previously published work describing the syntheses of other PEI derivatives.[12–14] Diamino compound ***4*** was prepared by nucleophilic substitution of two molecules of ***1*** by one molecule of ***2*** and subsequent reduction of the nitro groups to amines using Pd/C and hydrazine.

The 4,4′-[(3-methoxypropane-1,2-diyl)-bis(oxy)]dianiline ***4*** was isolated as a white powder in an overall yield of 68%. The diamine ***4*** is sensitive to air and light and becomes brownish within several days probably due to oxidation, especially in solution. The ^{1}H-NMR showed a 1:2 ratio



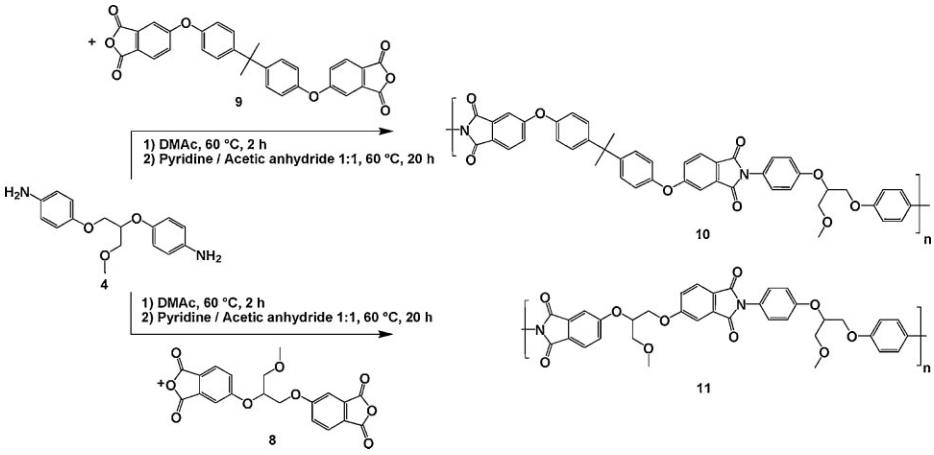
Scheme 1.
Synthesis of the monomers bearing 3-methoxy-1,2-propanediol.

between the aromatic protons and the introduced 3-methoxy-1,2-propanediol moiety like expected for coupling to the benzyl rings. The diamine ***4*** was analyzed for purity using the signal shape for T_m in DSC and verified a purity of 98.2%. Additionally to these analyses, the targeted structure was verified by ^{13}C-NMR, elemental analysis and mass spectrometry.

The synthesis of 4,4′-[(3-methoxypropane-1,2-diyl)bis(oxy)]bis(phthalic anhydride) ***8*** was performed in three steps by nucleophilic ipso substitution on 4-fluorophthalonitrile with ***2***, saponification to the free carboxylic acids in ***3***, and ring closure to the anhydrides. ***8*** was received as a brownish-grey powder in a yield of 65%. The ^{1}H-NMR signals corresponded to the expected 1:2 ration for the introduction of 3-methoxy-1,2-propanediol coupled to the phthalic anhydride parts. Purity analysis of the phthalic anhydride ***8*** by DCS was not suitable due to a missing melting point in the measured temperature region. As an indirect proof hydrolysis and measurements by ^{1}H-NMR was used. The phthalic anhydride was measured in DMF-d_7 first, then water was added to cleave the anhydride and finally measured again. In this way it was found that the signals for the aromatic protons shifted after hydrolysis back to the identical spectra found for the carboxylic acid precursor. As further methods, ^{13}C-NMR and mass spectrometry verified the composition of the targeted molecule.

Polymer Synthesis

Optimized reaction conditions and procedures were determined by performing experiments under varied conditions using 4,4′-(4,4′-isopropylidene diphenoxy)bis-(phthalic anhydride) ***9*** and 1,3-diaminobenzene (data not shown). In these experiments; (i) temperature (RT, 40 °C, 60 °C), (ii) reaction time before start of the imidisation with acetic anhydride/pyridine 1:1 v/v and (iii) addition of the comonomers (starting materials mixed at the beginning, drop wise addition of the diamine or phthalic anhydride in solution or as solid), were tested. It was found in these preliminary experiments that slow addition of the diamine (1 equivalent) to the dissolved phthalic anhydride (1.01 equivalents) at



Scheme 2.
Polymer syntheses routes.

60 °C and start of the imidisation after 2 h reaction time resulted in the highest number average molecular weights and lowest polydispersity as determined by GPC. With extended reaction times, the molecular weights started to decrease, which can be attributed to the equilibrium between the monomers and the amidic precursor formed. Therefore, all co-condensations were performed under these conditions.

Co-condensation of ***4*** with ***9*** (Scheme 2) resulted in a yellow copolymer ***10*** with $M_n = 6{,}400$ g/mol (PDI = 2.6). The polydispersity was elevated because of oligomeric fractions in the polymer. These fractions could not be separated by re-precipitation in methanol or other solvents (ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol and acetone). The ^{1}H-NMR (Figure 1) proofed a 1:1 ratio between both monomers after re-precipitation in methanol.

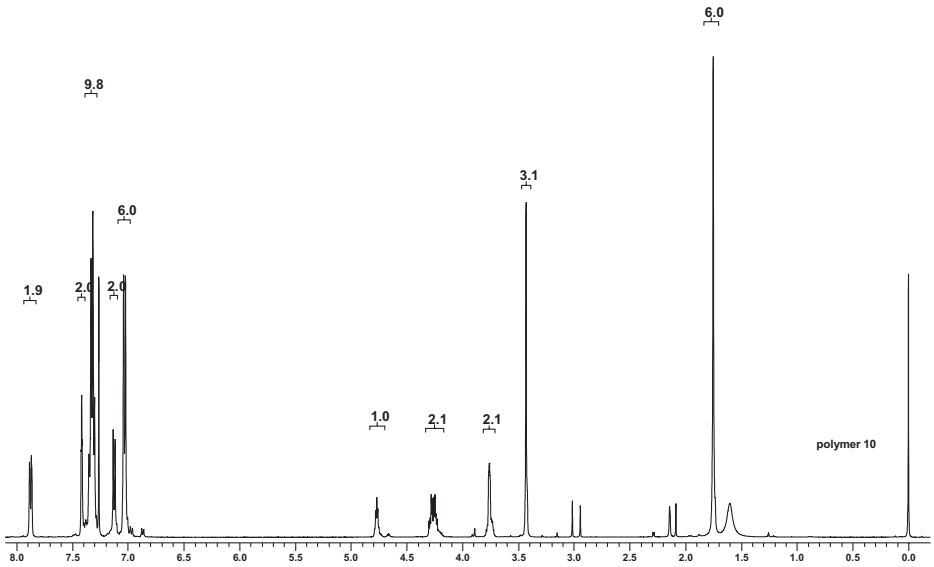


Figure 1.
^{1}H-NMR spectra of the polyetherimide polymer ***10*** in $CDCl_3$.

Table 1.
Contact angles, T_g, E-moduli, elongations at break ε_R and TGA data for the synthesised polymers 10, 11 and the standard.

Polymer	contact angle[a]			T_g[b]			mass loss of		E- modulus[c]	ε_R[c]
	Θ_{adv}	Θ_{rec}	hysteresis	Onset	Offset	Inflection	5%	10%		
	in°			in °C			at °C		in MPa	in %
10	76 ± 3	44 ± 3	32	157	163	160	439	457	1593	9
11	75 ± 1	58 ± 2	17	130	136	133	419	429	865	13
Ultem® 1000	84 ± 4	64 ± 2	20	214	219	216	525	535	1898	123

[a] n = 30; [b] determined by DSC; [c] tensile test, n = 5, room temperature.

The cast films had a contact angle (Table 1) of $\Theta_{adv} = 76° \pm 3°$. Compared to $\Theta_{adv} = 84° \pm 4°$ for polyetherimide from 4,4′-(4,4′-isopropylidenediphenoxy)-bis(phthalic anhydride) and 1,3-diaminobenzene a minor decrease in the hydrophobicity was achieved. Furthermore, the thermal properties (Table 1) were altered and a decrease in the T_g and decomposition temperature was determined. By introducing the 3-methoxy-1,2-propanediol in the diamine part, a $T_g = 160\,°C$ was found, which was already a decrease of ~50 °C compared to the commercial one. Interestingly, also the polymer decomposed at lower temperatures, although it is still highly heat resistant and the decomposition started at around 400 °C.

The number average molecular weight of polymer ***11*** consisting of ***4*** and ***9*** was determined to be $M_n = 3{,}700$ g/mol (PDI = 4.4) and a 1:1 ratio was found in ^{1}H-NMR (Figure 2), respectively.

The very high polydispersity could not be reduced by changing the temperature to 75 °C nor by reducing the reaction time to

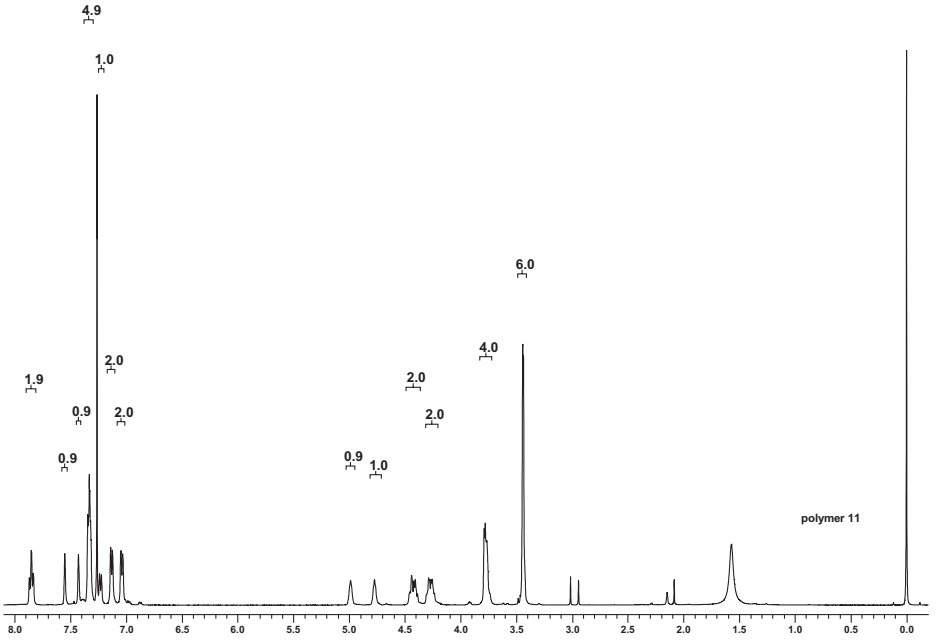


Figure 2.
^{1}H-NMR spectra of the polyetherimide polymer ***11*** in $CDCl_3$.

1 h before imidisation. Possibly an incomplete transfer of the carboxylic acid precursor to the phthalic anhydride ***8***, changed equilibrium between the amidic polymer precursor and the monomers or faster hydrolysis in the presence of unwanted water traces are reasonable for these findings. In the MALDI-TOF analysis of this polymer, the composition was further identified and the results indicated polymeric chains, which are end-capped with two moieties of the hydrolyzed anhydride ***8***. (Figure 3) Since the polymerisation was performed by drop wise addition of the diamine ***4*** to a minimal excess of the anhydride (1.01 eqiv.), this result is consistent with the targeted reaction process and expected.

The brown polymeric films showed a contact angle (Table 1) of $\Theta_{adv} = 75^\circ \pm 1^\circ$, which is not reduced further compared to the polymer ***10***. It seems that the hydrophilicity can be not mainly influenced by additional introduction of the 3-methoxy-1,2-propanediol in the second monomer unit. Potentially dimer- or trimer substituents of methoxy-propanediol are needed to further decrease the hydrophobic character of these polyetherimides.

In line with the findings of polymer ***10,*** the T_g (Table 1) was further decreased by introducing an additional 3-methoxy-1,2-propanediol bearing monomer. The T_g was 133 °C which is again a reduction of around 30 °C. In TGA again a high temperature resistance was determined. The decomposition of polymer ***11*** started around 400 °C.

The mechanical properties of the synthesised polyetherimides were tested by tensile tests at room temperature. In contrast to the original expectations, the T_g was not decreasing enough to get a completely flexible polymer at room temperature, so the material was measured in a glassy state. (Table 1). The polymer ***10*** had a reduced elongation at break compared to the commercial applied standard and only a slightly reduced E-modulus compared to the standard. For the polymer ***11*** the resistance to break was determined to be comparable to the values obtained for polymer ***10***, but the E-modulus decreased to ~ 870 MPa, which is a decrease of about 50% compared to the polymer ***11***.

The determined high E-moduli and low elongations at break can be attributed to the number average molecular weights and high polydispersity of the polymers, but partially also to the changed structures. First of all, the molecular weights were found to be lower than for the standard and the oligomeric parts further reduces the

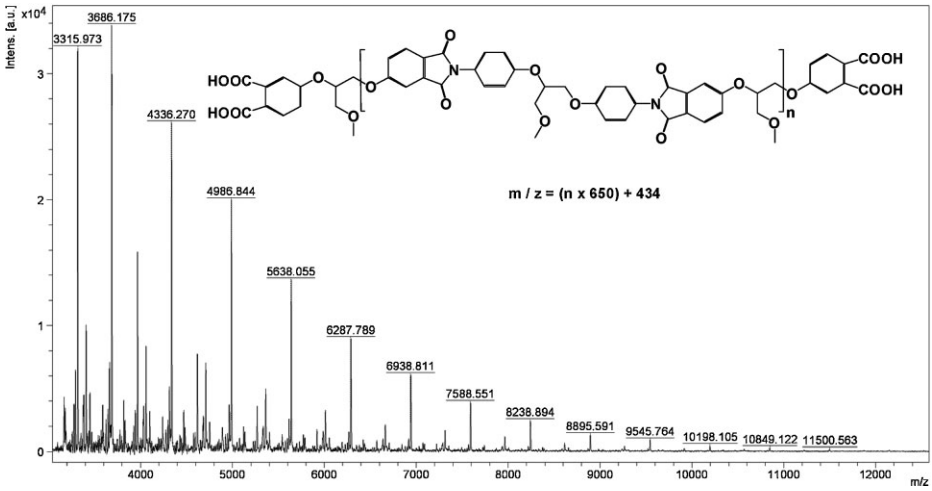


Figure 3.
MALDI-TOF mass spectra of polymer ***11***.

stability. Both facts are known to result in faster break at elongation. Secondly, the intermolecular chain interactions as one further parameter have to be considered in discussing the properties of polyetherimides. In literature, interactions of the aromatic moieties by charge transfer complex formation are reported.[11] The aromatic parts of the phthalic imide and the amine in the polymer chain are supposed to interact and form charge transfer complexes. The flexibility and distance between the aromatic rings influence the amount of potentially formed interactions. Having in mind that we introduced the 3-methoxy-1,2-propanediol as a more flexible moiety, we possibly enhance the interactions between the chains by easier arrangement of the chain parts. This often corresponds to the specific coloring (yellow to brown) of the polyimides, which was also found for our polymers.[14–15] To support these speculations, further experiments will have to be conducted to synthesis the polyetherimides without oligomeric fractions and complete comparable molecular weights.

Conclusion

Polyetherimides with introduced 3-methoxy-1,2-propanediol moieties were successful synthesized. A synthesis strategy for the required monomers was developed, and the monomers could be synthesized in overall yields of 65%. The polymers synthesized from 4,4′-[(3-methoxypropane-1,2-diyl)bis-(oxy)]dianiline and 4,4′(4,4′–iso-propylidene-phenoxy)-bis-(phthalicanhydride) ***10*** ($M_n = 6{,}400$ g/mol, PDI = 2.6) as well as from 4,4′-[(3-methoxypropane-1,2-diyl)bis(oxy)]-dianiline and 5,5′-[(3-methoxypropane-1,2-diyl)bis(oxy)]-bis(phthalic anhydride) ***11*** showed a slight tendency to reduced contact angles compared to polyetherimide from 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride) and 1,3-diaminobenzene. Both synthesized polymers were thermally stable up to 400 °C. Introducing the methoxyglycerole unit in the diamine monomer resulted in lowering of T_g to 160 °C and to $T_g = 133$ °C by introducing both comonomers. The flexibility of the polymer chains was not strongly enhanced according to tensile tests. While for the introduction of the diamine ***4*** the E-modulus was only reduced by 200 MPa compared to the standard, for the polymer with both new comonomers the E-modulus decreased about 50% to 870 MPa.

Acknowledgements: We thank Mrs. I. Starke in the Department of Analytical Chemistry (University of Potsdam) for measuring the mass spectra and performing the elemental analysis of the monomeric compounds.

[1] F. Jung, C. Wischke, A. Lendlein, *MRS Bull.* **2011**, *35*, 607–613.
[2] Y. Feng, M. Behl, S. Kelch, A. Lendlein, *Macromol. Biosci.* **2009**, *9*, 45–54.
[3] G. Tronci, A. T. Neffe, B. F. Pierce, A. Lendlein, *J. Mater. Chem.* **2010**, *20*, 8875.
[4] J. Zotzmann, M. Behl, Y. Feng, A. Lendlein, *Adv. Funct. Mater.* **2010**, *20*, 3583–3594.
[5] A. T. Neffe, A. Zaupa, B. F. Pierce, D. Hofmann, A. Lendlein, *Macromol. Rapid Comm.* **2010**, *31*, 1534–9.
[6] J. Vienken, S. Bowry, *Artif. Organs* **2002**, *26*, 152–9.
[7] D. G. Ebo, J. L. Bosmans, M. M. Couttenye, W. J. Stevens, **2006**, 61, 211–220.
[8] Y. Imai, A. Watanabe, E. Masuhara, *J. Biomed. Mater. Res.* **1983**, *17*, 905–12.
[9] R. R. Richardson, J. Miller, W. M. Reichert, *Biomaterials* **1993**, *14*, 627–35.
[10] S. Braune, M. Lange, K. Richau, K. Lützow, T. Weigel, F. Jung, A. Lendlein, *Clin. Hemorheol. Micro.* **2010**, *46*, 239–50.
[11] C. J. Lee, *Polym. Rev.* **1989**, *29*, 431–560.
[12] G. C. Eastmond, J. Paprotny, *Macromolecules* **1996**, 1382–1388.
[13] G. C. Eastmond, J. Paprotny, R. A. Pethrick, *Macromolecules* **2006**, 7534–7548.
[14] C.-P. Yang, S.-H. Hsiao, H.-W. Yang, *Macromol. Chem. and Phys.* **2000**, *201*, 409–418.
[15] R. A. Dine-Hart, W. W. Wright, *Makromol. Chem.* **1971**, *143*, 189–206.

