Polyphenylsulfone (PPSU) plastic for baby bottles:

an example for a comprehensive analytical NIAS assessment based on polymer-related extractables and leachables.

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Introduction

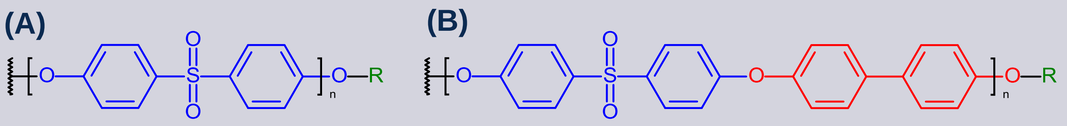
Since polycarbonate basically consisting of bisphenol A (BPA) was banned for the production of baby bottles, the polyarylsulfone plastics **polyethersulfone (PES)** and **polyphenylsulfone (PPSU)** became promising alternatives. PES and PPSU are extremely resistant materials to chemical (acids/bases), mechanical and thermal treatments. PES and PPSU are formally composed of **bisphenol S (BPS)** as well as **4,4'-dihydroxybiphenyl (DHBP)**. Based on their bisphenolic molecular structure, both substances might cause similar endocrine effects compared to the banned BPA.

In our study, we analyzed commercially available PES and PPSU materials used for baby bottles. We focussed on the identification and quantification of polymer related substances, mainly monomer derivatives as well as oligomers with a molecular weight below 1.000 dalton, as potential migrants into baby food.

Polymer production and structures

Polyarylsulfones like PES and PPSU are usually prepared by polycondensation of the chlorinated BPS derivative 4,4'-dichloro-diphenylsulfone (short Cl-BPS-Cl) with BPS (PES) or DHBP (PPSU) in an aprotic polar solvent such as N-methylpyrrolidine (NMP) or sulfolane.

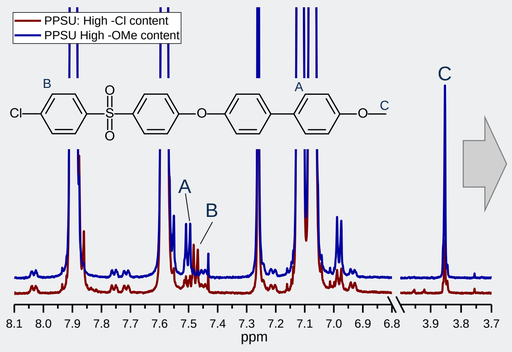
By final addition of chloromethane, the hydroxyl end groups of the linear polymer chains are partially methoxylated.



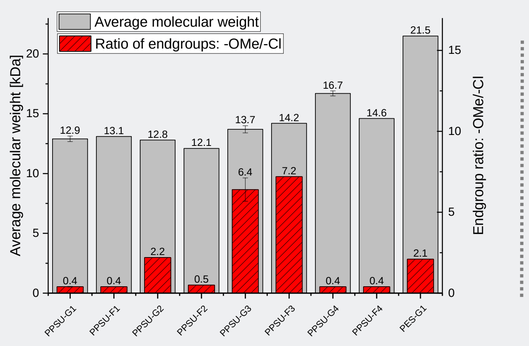
Polymer structures of PES (A) and PPSU (B). PES exclusively consists of repeating units of BPS, whereas BPS and DHBP units alternate in the PPSU polymer. Polymer end groups –R can be hydroxylated (–OH), chlorinated (–Cl) or methoxylated (–OMe).

► Total polymer characterization

^{1}H-NMR → Average molecular weight & analysis of end groups

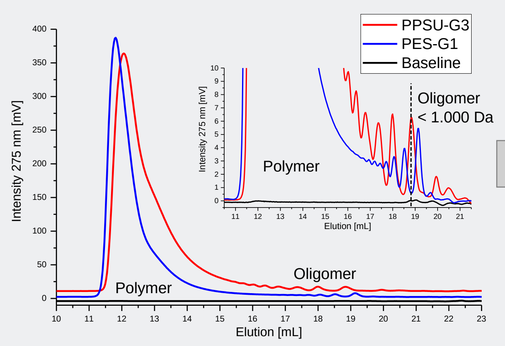


1H-NMR (600 MHz) of completely dissolved PPSU polymers in CDCl3. Determination of average molecular weight and ratio of endgroups (-OMe/-Cl).

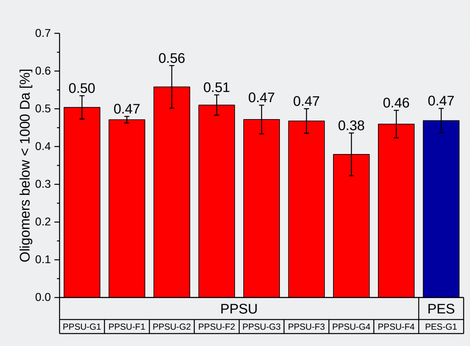


Results of 1H-NMR analysis. Minor differences in average molecular weight, but big differences in the ratio of methoxylated (-OMe) and chlorinated (-Cl) endgroups.

HPLC-SEC → Oligomers below 1.000 dalton



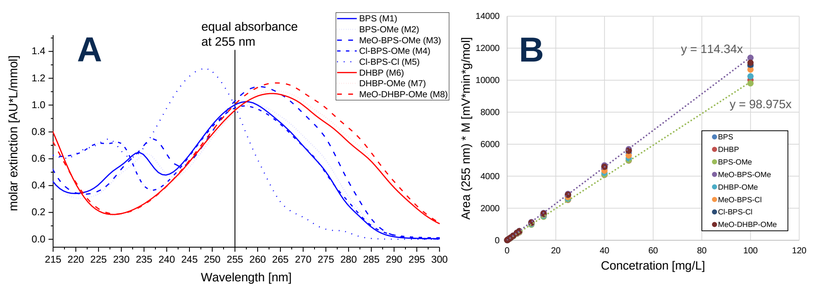
Size exclusion chromatography (HPLC-SEC) of completely dissolved polymers. Estimation of relative oligomer content below 1.000 dalton.



Relative oligomer content < 1.000 dalton determined by HPLC-SEC. Minor differences between the polymers. Average oligomer content ~ 0.5 %.

► Identification and determination of linear and cyclic PES/PPSU oligomers after solvent extraction

Oligomer quantification: Chromophore concentration



A) UV spectra of commercially available as well as self-synthesized chlorinated and methoxylated monomer derivatives of DHBP and BPS. Almost equal molar absorbance (± 7%) of all derivatives at 255 nm. Usage of 255 nm as specific wavelength for quantification of linear and cyclic PES/PPSU oligomers based on the chromophoric concentration as reported by SCHÄFER[1].

B) Linear calibration curves of all monomer derivatives of BPS and DHBP at the common wavelength of 255 nm. Usage of the linear regression curve of the commercially available reference substance BPS for the quantification of PES/PPSU oligomers.

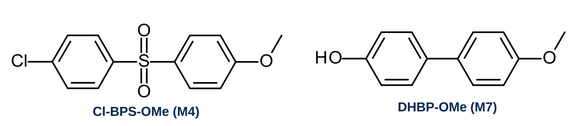
Chromophore concentration

$$c_c = c_s \cdot \frac{n}{M_w}$$

c_c: *Chromophore concentration* $[\mu mol \cdot L^{-1}]$ — n: *Number of aromatic rings in oligomer structure*

c_s: *Oligomer concentration* $[\mu g \cdot L^{-1}]$ — M_w: *Molecular weight of the oligomer* $[g \cdot mol^{-1}]$

C



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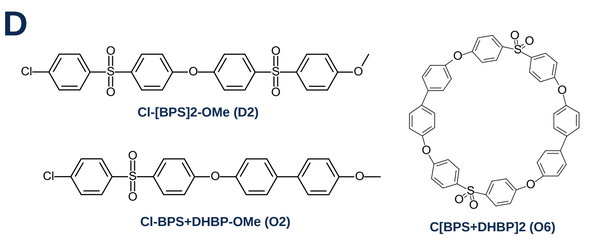
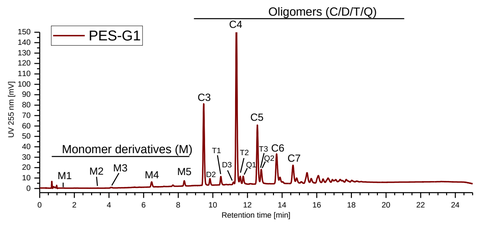


C) Structural examples of monomer derivatives (Mx) of BPS and DHBP with chlorinated, methoxylated and hydroxylated end groups.

D) Structural examples of linear and cyclic PES (Dx) und PPSU oligomers (Ox).

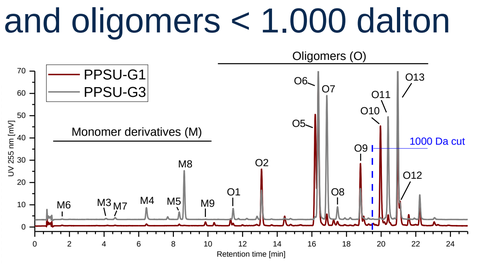
Extracts: Monomer derivatives and oligomers < 1.000 dalton



RP-HPLC chromatogram (UV 255 nm) of a milled PES material after solvent extraction (conditions: acetonitrile, 1h, 120°C).

Table: Extraction results of milled PES-1 material after extraction with different solvetns (ACN, EtOH, 50% EtOH, each 1h, 120°C).

#	Typ	Struktur	M [g/mol]	ACN, 1h, 120°C [mg/kg]	EtOH 1h, 120°C [mg/kg]	50% EtOH 1h, 120°C [mg/kg]
M1	Monomer	BPS	250.3	~ 0.3 (NWG)	~ 0.3 (NWG)	~ 0.3 (NWG)
M2	Monomer	BPS-OMe	264.3	2	1	0.5
M3	Monomer	MeO-BPS-OMe	278.3	20	6	2
M4	Monomer	Cl-BPS-OMe	282.7	111	48	14
M5	Monomer	Cl-BPS-Cl	287.1	184	53	11
C3	Cyclic	C[BPS]3	696.8	854	148	39
C4	Cyclic	C[BPS]4	929.1	2483	357	52
C5	Cyclic	C[BPS]5	1161.4	969	119	10
D1	Linear	MeO-[BPS]2-OMe	510.8	n.A.	n.A.	n.A.
D2	Linear	Cl-[BPS]2-OMe	515.0	122	36	8
D3	Linear	Cl-[BPS]2-Cl	519.4	33	12	3
T1	Linear	MeO-[BPS]3-OMe	742.8	149	36	8
T2	Linear	Cl-[BPS]3-OMe	747.2	143	34	6
T3	Linear	Cl-[BPS]3-Cl	751.7	n.A.	n.A.	n.A.
Q1	Linear	MeO-[BPS]4-OMe	975.1	n.A.	n.A.	n.A.
Q2	Linear	Cl-[BPS]4-OMe	979.5	n.A.	n.A.	n.A.



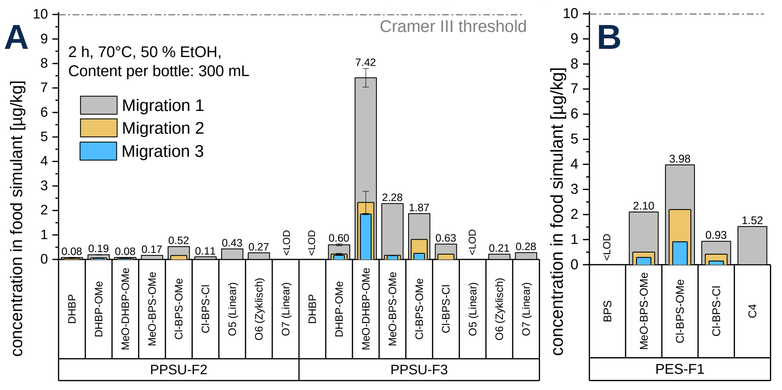
RP-HPLC chromatograms (UV 255 nm) of two milled PPSU materials after solvent extraction (conditions: acetonitrile, 1h, 120°C).

Table: Total extraction of monomer derivatives and oligomers from three different PPSU materials. Each 10 times consecutive acetonitrile, 1h, 120°C.

#	Typ	Struktur	M [g/mol]	PPSU-G1 [mg/kg]	PPSU-G2 [mg/kg]	PPSU-G3 [mg/kg]
M6	Monomer	DHBP	186.2	2	2	3
M3	Monomer	MeO-BPS-OMe	278.3	n.A.	1	4
M7	Monomer	DHBP-OMe	200.2	2	7	12
M4	Monomer	Cl-BPS-OMe	282.7	10	14	70
M5	Monomer	Cl-BPS-Cl	287.1	9	8	31
M8	Monomer	MeO-DHBP-OMe	214.3	2	10	195
M9	Monomer	Biphenyl	154.2	11	n.d.	n.d.
O6	Cyclic	C[BPS+DHBP]2	801.0	1241	1406	971
O1	Linear	MeO-[BPS+DHBP]-OMe	446.5	16	94	42
O2	Linear	Cl-[BPS+DHBP]-OMe	450.9	284	216	151
O5	Linear	Cl-[BPS+DHBP+BPS]-Cl	687.6	712	245	11
O7	Linear	MeO-[DHBP+BPS+DHBP]-OMe	614.7	62	485	639
O8	Linear	MeO-[BPS+DHBP]2-OMe	846,9	31	204	70
O9	Linear	Cl-[BPS+DHBP]2-OMe	851,4	397	281	187
O10	Linear	Cl-[BPS+DHBP]2+BPS-Cl	1088.1	822	281	5
O11	Linear	MeO-[DHBP+BPS]2+DHBP-OMe	1015.2	90	636	809
O13	Linear	MeO-[DHBP+BPS]3+DHBP-OMe	1415.6	n.A.	n.A.	n.A.

► Migration into food simulants

50% ethanol in water, 2h, 70°C, 3 times consecutive



Results of migration tests according to EU (VO) 10/2011. 3 times consecutive migration into 50% EtOH (2h, 70°C). Migration of monomer derivatives as well as oligomers from PPSU (A) and PES (B) bottles. (LOD: ~0.1 µg/kg).

► Risk assessment

Specific migration limit (SML) EU (VO) 10/2011 *		NIAS evaluation according to Threshold of Toxicological Concern (TTC)	
BPS (M1)	50 µg/kg food simulant	Not listed monomers	10 µg/kg food simulant **
Cl-BPS-Cl (M5)		Linear oligomers	
DHBP (M6)	6 mg/kg food simulant	Cyclic oligomers	

* ***Specific migration limit (SML). Evaluation of the third migration after three times consecutive migration into food simulant for milk (50% ethanol, 2h, 70°C).***

** ***Evaluation of not listed (10/2011) monomer derivatives of BPS and DHBP as well as the linear and cyclic oligomers based on the TTC concept (TTC threshold for Cramer III substances: 1.5 µg/kg bw & day).***

Calculation of Cramer III threshold based on EFSA[2]: 3 kg baby bodyweight, daily intake: 150 mL/kg bw → Cramer III threshold: 10 µg/kg food simulant.

Conclusion

- **PES and PPSU polymers from different manufacturers were characterized by ^{1}H-NMR, size exclusion chromatography and RP-HPLC analysis with respect to their end groups, their average molecular weight and their oligomer content < 1.000 dalton.**
- **PES and PPSU oligomers were identified by LC-ESI(+)-MS and (semi-) quantified based on the chromophore concentration using the commercially available reference substance BPS at a specific UV-wavelength.**
- **Migration tests according to EU (VO) No. 10/2011 with food simulant for milk (50% EtOH) were performed. Neither SML values for listed monomers nor TTC thresholds for not listed monomers and oligomers were exceeded.**
- **Based on our studies, baby bottles made from PES or PPSU materials can be evaluated as safe alternatives for polycarbonate with regard to the migration of polymer related substances.**

References

Data published: Eckardt et al., 2018. Food Addit Contam Part A. DOI: 10.1080/19440049.2018.1449255

[1] Schaefer et al., 2004. DOI 10.1080/02652030310001637939

[2] EFSA 2016. DOI: 10.2903/j.efsa.2016.4357

Publication

Poster online

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