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Synthesis and Characterisation of Branched Polyarylethers

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Summary: Polyarylethers (Polysulfone: PSU, Polyethersulfone: PES) belong to the group of high performance polymers, having high glass transition temperature as well as high continuous use temperature. As a consequence of their high glass transition temperature, these polymers display high melt viscosity, which limits the number of accessible applications. Since the conventional methods to improve the flow characteristics are limited, the influence of branching by incorporation of the tri-functional monomer 1,1,1-Tris-(4-hydroxyphenyl)ethane (THPE) on the flow and the mechanical performance of PES was studied.

Branching enhances the flow of Polyethersulfone significantly, but has a deleterious effect on the toughness, especially Charpy impact and tensile elongation.

Keywords: branching, mechanical properties, melt flow, polyarylethers

Introduction

Polyarylethers (Polysulfone: PSU, Polyethersulfone: PES) belong to the group of high performance polymers, having high glass transition temperature as well as high continuous use temperature.[1-4] These materials are widely used in high end applications, like dialysis membranes, head lamp reflectors, and microwave cookware.[5-7]

As a consequence of their high glass transition temperature (PSU: 186°C, PES: 225°C), these polymers have comparatively high melt viscosity. Subsequently, processing of large parts or of parts with low wall thickness very often causes severe problems. This issue limits the number of accessible applications significantly.

As known from the literature, branched polymers usually display better flow performance than linear products with comparable molecular weight.[8] Especially in the area of Polyolefines, branching is a powerful tool to tailor flow and processing behaviour.[9] Also in the case of Polyamides, branching nowadays is used to improve the processing behaviour, especially the cycle time in injection moulding processes.[10] The improvement of the melt

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flow without changing other positive properties of Polyarylethers would enhance the market potential of these materials significantly.

The common ways to improve the melt flow of thermoplastic materials, like the addition of flow promoters e.g. waxes, mineral oils or stearates, have limited impact in the case of polyarylethers, due to problems like dispersion of low viscosity additives in the highly viscous melt, or reduction of the transparency, or thermal degradation of the additive and subsequent discoloration of the product. blending of polyarylethers with liquid crystalline polymers (LCP) gives nice improvements of the processing behaviour, but the obtained mixtures suffer from bad toughness, even at very small loading of LCP.[11,12]

The melt flow of polyarylethers can be significantly improved by blending with engineering plastics like Polyamides or polycarbonates.[13,14] But in all cases, the obtained blends are opaque as a consequence of their phase separated morphology.

As already discussed, branching should improve the melt flow of polyarylethers. By incorporation of a small amount of a heat resistant molecule as branching unit, no deleterious influence on the thermal stability and transparency should be observed. Since the molecular weight for entanglements (M_e) is quite low in the case of polyarylethers (appr. 2000 g/mol),[15] the mechanical properties of branched products are expected to remain within the limits known for linear products. Thus, branched polyarylethers were synthesised and characterised.

The synthesis of such products is already described in the patent literature, but limited information about the influence of branching on the mechanical performance of polyarylethers is available up to now.[16]

Generally, polyarylethers are prepared via nucleophilic polycondensation starting from di-chloro and di-hydroxy-components.[4,17] For the synthesis of polyethersulfone, dichloro-diphenylsulfone (DCDPS) and dihydroxydiphenylsulfone (DHDPS) are used as monomers. Using a tri-functional unit, like 1,1,1-Tris-(4-hydroxyphenyl)ethane (THPE, Figure 1) as co-monomer, branching is possible. This product (THPE) is commercially available and soluble in the reaction mixture. The reaction scheme for the synthesis of the branched polyethersulfone is depicted in Figure 1. This procedure can also be used to synthesise unique branched polysulfones, having anhydride end-groups as compatibilizer for PSU/PA-alloys.

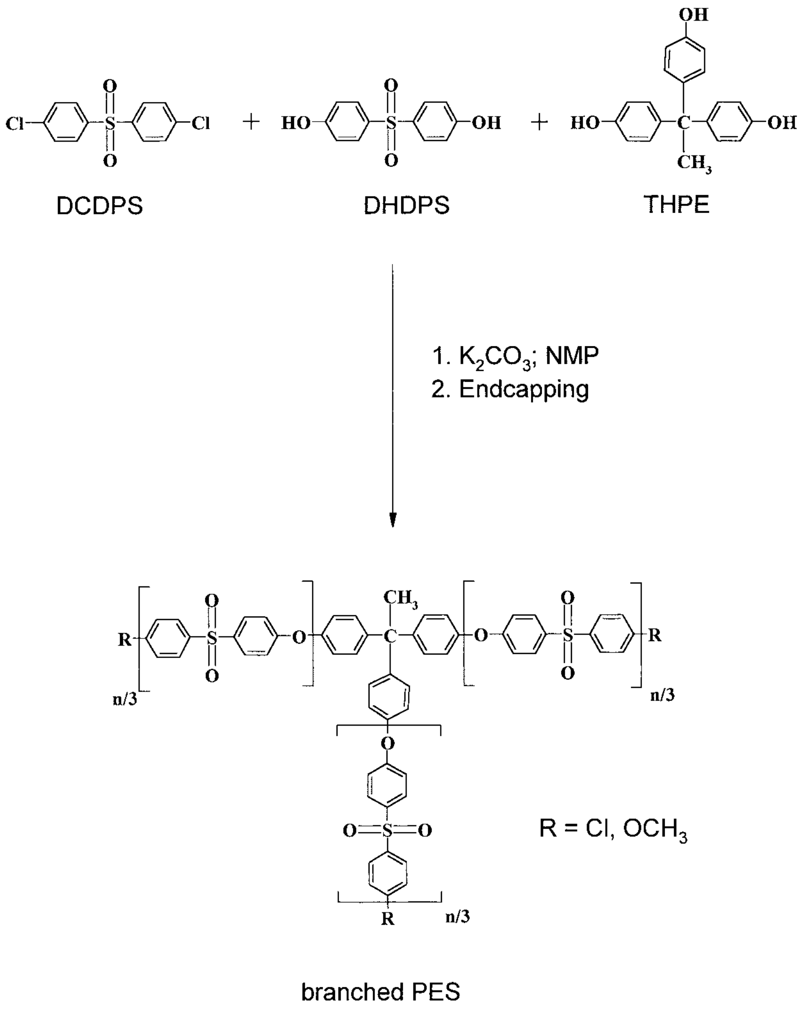

Fig. 1. Reaction scheme for the synthesis of branched polyethersulfone.

Results and Discussion

Branched Polyethersulfones

Using a standard process for the preparation of Polyethersulfone (1 mol monomers in 1000 ml N-methylpyrrolidone (NMP), 1 mol K_2CO_3, 6h 195°C), products with THPE amounts from 0,5 to 3 mol-% were prepared. In the first experiments, the ratio between OH- and Cl-end-groups was not adjusted. After a condensation time of 6 h the products were isolated by precipitation in water and characterised. As can be seen from Figure 2, the viscosity number (V.N., determined at 25°C, 0,5 g product in 100 ml NMP), as a measure for the molecular weight of the obtained products, decrease with increasing amount of charged THPE as a consequence of the stochiometric ratio. The scattering of the data might be due to differences in the reaction conditions (monomer purity, heating rate, etc.).

The amount of incorporated THPE in the obtained branched polyethersulfones (PES-b) can be determined by ^{1}H-NMR-spectroscopy (Figure 3). The protons of the methyl group of THPE can be used to calculate the amount of incorporated THPE. The obtained data (Table 1) indicate, that only 70 % of the charged THPE is incorporated into the branched polyethersulfons.

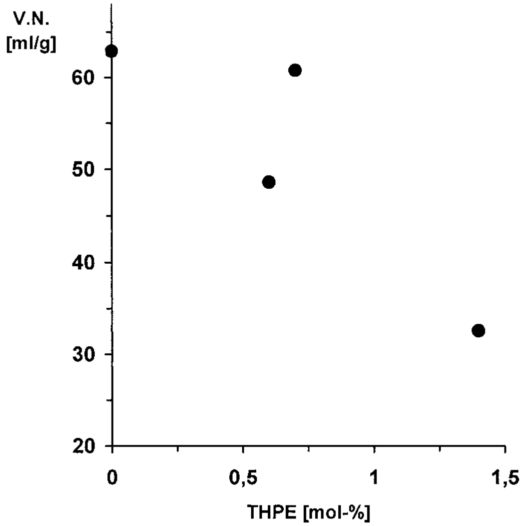

Fig. 2. Viscosity number as a function of incorporated THPE in branched PES.

The product with the THPE-content of 0,7 mol-% and the linear PES have almost the same viscosity number (Figure 2), subsequently these two samples were used for rheological measurements. Using a capillary rheometer, the apparent melt viscosity as a function of shear rate was determined for these two products at 350°C (Figure 4).

Table 1. Results of the characterisation of branched PES.

Product*	THPE [mol-%]		V.N.	Tg
	charged	found	[ml/g]	[°C]
PES	---	---	62,9	229
PES-b1	0,5	0,6	48,6	223
PES-b2	1	0,7	60,8	226
PES-b3	2	1,4	32,6	215
PES-b4	3	n.b.	non soluble	n.b.

* 6h condensation time

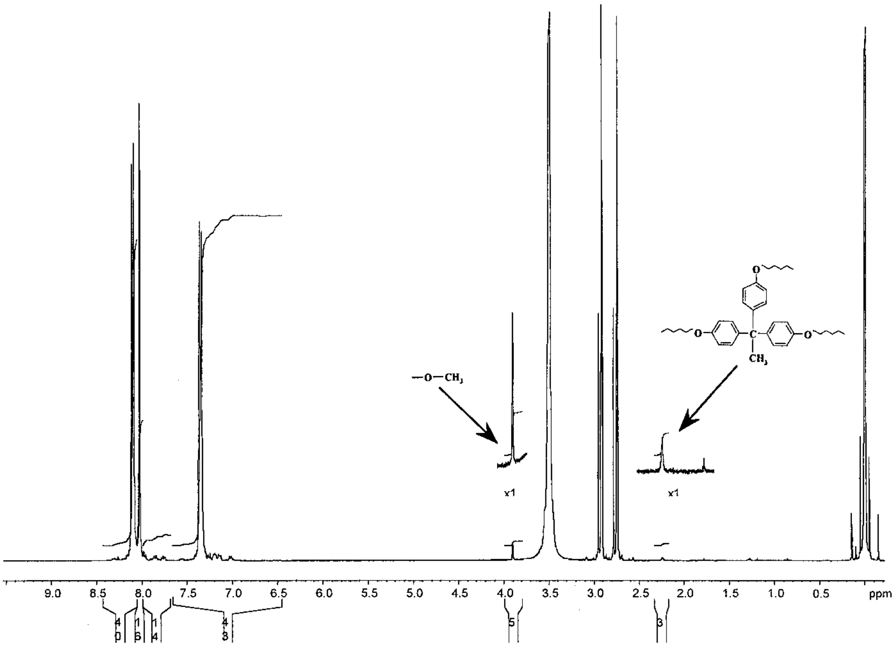

Fig. 3. ^{1}H-NMR-spectrum of PES-b2 (d_6-DMF as solvent), δ= 2,3 ppm: CH_3 of THPE unit, δ=3,9 ppm: CH_3 of Methoxy-endgroups .

As can be clearly seen from Figure 4, the branched product has a lower melt viscosity as the linear product with the same viscosity number. From these small-scale trials it was concluded, that the desired reduction of the melt viscosity could be achieved by incorporation of THPE.

In order to have enough material for mechanical testing, branched PES-samples were prepared on a 1 kg-scale. To have a better control of the reaction, the stochiometric ratio between the di-chloro and the hydroxy-monomers was adjusted to be 1/1 in these experiments. The amount of charged THPE was again varied from 0 to 3 mol-%. The reaction time was adjusted according to the THPE-content. The obtained polymers were isolated by precipitation in water. After drying, the powders were compounded on a Prizm PTW 16 extruder to yield granulates. The barrel temperature was set at 350 °C; the throughput was 1 kg/h at a screw speed of 200 rpm.

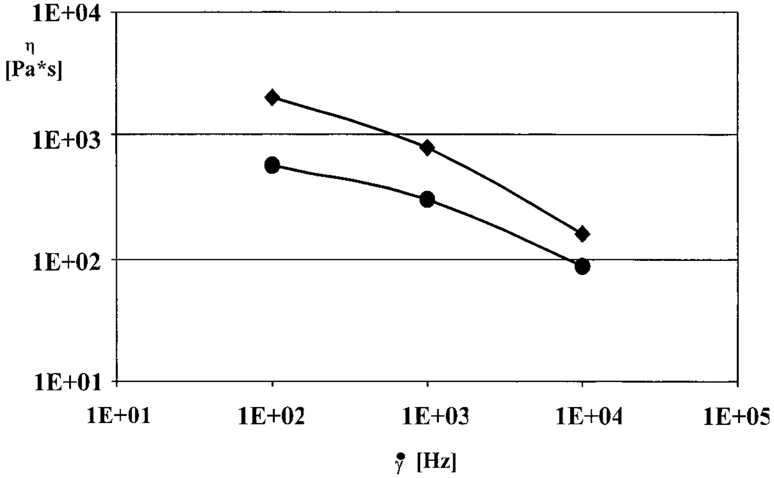

Fig. 4. Flow curves of a linear ▲ (PES) and a branched • (0,7 mol-% THPE, PES-b2) Polyether-sulfone at 350°C.

From the granulates ISO-samples for impact (Charpy impact: ISO 179 1eU, Charpy notched impact: ISO 179 1eA), tensile testing (ISO 527) and Vicat B (ISO 306) measurements were injection moulded at a melt temperature of 350°C and a mould temperature of 120°C.

The viscosity number and the THPE-content of the obtained products are summarised in Table 2.

Table 2. Results of the characterisation of branched PES.

	Condensation time [h]	THPE [mol-%]		V.N. [ml/g]
		charged	found	
PES	3,5	0	0	44,8
PES-b5	3,75	1	0,7	44,7
PES-b6	3	2	1,5	44,6
PES-b7	3,5	2	1,5	64,8
PES-b8	4	2	1,6	88,9

Three products obtained after different reaction times have almost the same viscosity number (45 ml/g). The properties of these three samples can be compared to study the influence of the amount of incorporated THPE on the mechanical performance. It can be clearly seen, that the incorporation of THPE has almost no influence on the Vicat B softening temperature and the E-modulus (Figure 5a and b), while the toughness is dramatically reduced by the incorporation of the branching units (Figure 6a and b). Especially the Charpy impact shows an immediate drop to a level below the 50% value of the linear product with the same viscosity number. In the case of the notched impact, a decrease of the toughness with increasing amount of THPE was also observed.

From comparative trials with linear PES the influence of the viscosity number on the toughness of PES was known. Below a viscosity number of 40 ml/g a tremendous reduction of the toughness occurs (Figure 7a). Since the samples discussed have only a slightly higher viscosity number than 40 ml/g, the influence of the viscosity number on the mechanical performance at a fixed THPE-amount was studied as well.

For the products with about 1,5 wt.% THPE (Table 2), only a slight dependence of the Charpy impact with increasing viscosity number is visible (Figure 7a). The level of the linear products is not achieved, even at very high viscosity number.

For the Charpy notched impact a significant increase of the toughness with increasing viscosity number was observed (Figure 7b). For a high viscosity number (> 65 ml/g), the toughness level of linear products was achieved.

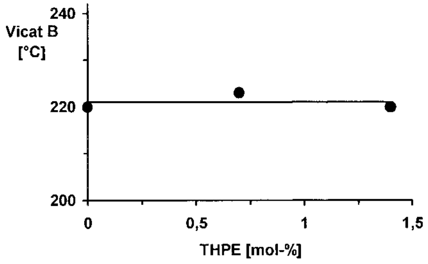

Fig. 5a.Vicat B softening temperature as a function of the THPE-content for PES.

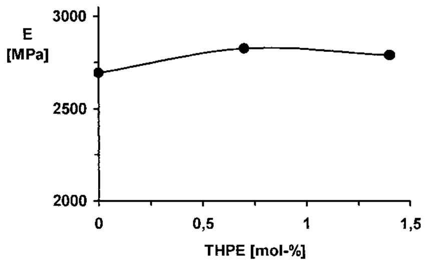

Fig. 5b. E-Modulus as a function of the THPE-content for PES.

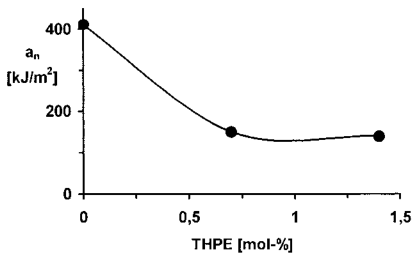

Fig. 6a. Correlation between the Charpy impact toughness and the THPE-content for PES.

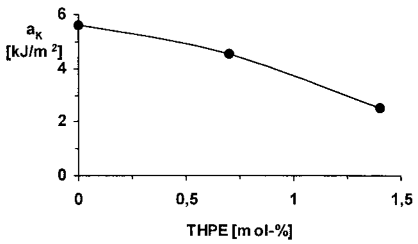

Fig. 6b. Correlation between the Charpy notched impact toughness and the THPE-content for PES.

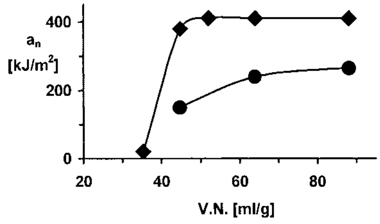

Fig. 7a. Relationship between Charpy impact toughness and viscosity number for linear and branched PES (1,5 mol-% THPE).

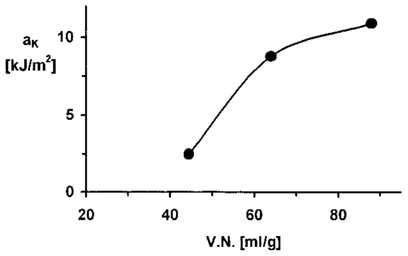

Fig. 7b. Relationship between the Charpy notched impact and viscosity number for branched PES (1,5 mol-% THPE).

In the Charpy impact test without notch, the energy to initiate a crack as well as the energy to drive the crack through the material is characterised. Since the difference between linear and branched PES is less pronounced in the Charpy notched impact, the observed behaviour in the Charpy impact is mainly related to the crack initiation. Polyarylethers usually belong to the group of pseudo-ductile polymers having a high entanglement density[15]. The observed reduction in toughness can thus be explained in terms of a reduced entanglement density as a consequence of the branching and a higher M_e-value. On the other hand it has to be mentioned, that due to the low molecular weights of these products (M_n appr. 6000 - 12000 g/mol) and the low amounts of incorporated THPE, not every chain has one branching unit.

Conclusions

The incorporation of 1,1,1-Tris-(4-hydroxyphenyl)ethan (THPE) in the Polyethersulfone chain leads to branched materials with reduced melt viscosity compared to linear material with a comparable viscosity number. ^{1}H-NMR reveals that only about 70 % of the THPE is incorporated in the obtained product. As a consequence of the THPE-incorporation, the toughness of the branched PES is significantly lower than for linear material. Especially the Charpy impact and the tensile elongation of branched PES are pretty low. Branched PES with high viscosity number on the other hand has the same notched impact strength as linear products. Branching obviously disturbs the entanglement of the PES-chains, enhancing the sensitivity for crack formation.

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