Star-shaped poly(2,6-dimethyl-1,4-phenylene ether)

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Summary

The properties of star-shaped poly(2,6-dimethyl-1,4-phenylene ether) (PPE), as prepared by the redistribution of PPE and tyrosine-modified poly(propylene imine) dendrimers, are studied in solution and in 50/50 wt% blends with linear polystyrene. Star polymers with constant armlength but increasing number of arms show the same hydrodynamic volume as measured by Size Exclusion Chromatography (SEC), but decreasing hydrodynamic radius as measured by Dynamic Light Scattering (DLS). This is caused by the restricted mobility of the more densely packed chains at high numbers of arms, also leading to a decrease in intrinsic viscosities. These solution properties are also reflected in the miscibility behaviour in polymer blends. Star-shaped polymers with a high number of PPE arms (16,32 or 64 respectively) give inhomogeneous blends with linear polystyrene, in contrast to the miscible combination of linear polystyrene with linear PPE or star-shaped polymers with a low number (4 or 8) of PPE arms.

Introduction

Star-shaped polymers are gaining interest because of their characteristic rheological properties and their dilute-solution properties (1). The interest for branched polymers, in general, arises from their compactness and enhanced segmental density as compared to their linear counterparts of the same molecular weight. Therefore, the star-shaped polymers resemble more closely the hard-sphere model than linear polymers, especially when the number of arms in the star polymer increases (2). Besides the higher segmental density, star-shaped polymers and linear polymers also differ in shape (3). Although the orientationally averaged shape of each macromolecule in free space is spherical, the instantaneous shape of linear polymers will be ellipsoidal and that of star polymers tends to become more spherical. The hard-sphere character of the star polymers is directly correlated to the degree of dynamic entanglements. By an increase of the number of arms, the degree of dynamic entanglements decreases for star-shaped polymers and is substantially lower than that of linear chains. This causes a lower intrinsic viscosity of star polymers as compared to linear polymers of the same molecular weight. The dynamics of entangled polymers is well described by the reptation model, however, reptation for star molecules is strongly suppressed due to the star centre.

Phase-separation in blends of linear polymers has been investigated widely (4). Dynamics and phase behaviour of polymer blends made out of linear and star-shaped polymers is studied mainly theoretically (5). As theoretically predicted, polymer branching directly affects miscibility and, therefore, also morphology and mechanical properties. However, only a few experimental studies are reported, and most of them describe mixtures of branched polymers with their linear counterpart. Roovers (6) and Struglinski (7) studied the viscoelastic properties and relaxation behaviour of binary mixtures of linear and star polybutadienes, while the liquid-liquid phase separation in binary blends of branched polyethylenes with linear polyethylenes is described in detail (8). Phase-separation kinetics of mixtures of linear and star-shaped polymers of different nature have been studied experimentally for star-shaped polystyrene and linear poly(vinyl methyl ether) (9). In this case, however, the corresponding mixtures of their linear polymers already show phase separation. The minimum of the cloud-point curve of the star/linear system is several degrees lower in comparison to the linear/linear system. Hence, the star/linear blend shows phase separation already at lower temperatures. Hardly any investigations are reported on phase separation in linear/star polymer blends, using polymers that give homogeneous blends of their linear analogues. By mixing both linear and star-shaped poly(ε-caprolactam) (PCL) with styrene-acrylonitrile copolymers (SAN) miscible blends can be produced, which show one glass transition temperature. However, it appears that only a fraction of the PCL chains is miscible with the SAN resulting in moderately elevated glass-transition temperatures (10). The SAN chains are unable to penetrate in an efficient manner into the core region. This is consistent with a model of an impermeable core from which the arms of the star diffuse outward (11). In this miscibility study a 6-arm star PCL is used. Increasing the number of arms will probably give a more pronounced phase-separation.
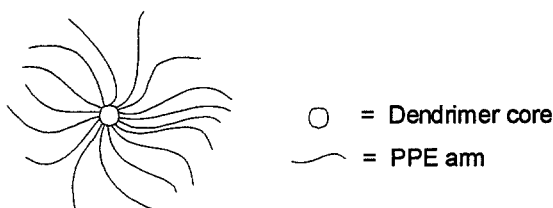

○   = Dendrimer core

⌒   = PPE arm

Figure 1: Schematic representation of a star polymer

In general, the influence of the number of arms of star-shaped polymers on the phase behaviour of blends with linear polymers has not been studied to a large extent. The blends of linear PS and linear PPE were recognized as being homogeneous at all compositions (12), however some microhetereogeneities can be detected by solid state NMR (13) and pressure can cause phase separation of this blend (14). Recently, we have been able to prepare star-shaped poly(2,6-dimethyl-1,4-phenylene ether) (PPE) with facile control of the number of PPE arms (15), as schematically shown in Figure 1. As core, we used well-defined poly(propylene imine) dendrimers (16), with an exact number of end groups varying from 4, 8, 16, 32 to 64. After a modification with protected amino acids, like *tert*-butyloxycarbonyl (tBOC) protected phenylalanine or tyrosine, a rigid shell is obtained (17). These dendrimers have been used as dendritic box for encapsulation of guest molecules. Because of their well-defined structure and rigid shell, these dendrimers are very useful in star polymers as a conformationally frozen core with a well-defined

number of end groups. The tyrosine-modified dendrimers, which have phenolic end groups, are reactive in a redistribution reaction with PPE to give star-shaped PPE (Figure 2). The arm length of the star-branched PPE is easily regulated by the employed phenol/PPE ratio. These star polymers with a well-defined number of arms will be ideal model compounds to study miscibility of linear/star blends. The aim of this research is the investigation of the miscibility behaviour of these star polymers with linear polystyrene (PS) with variation of the number of arms of the PPE star polymer.

Experimental
Techniques
Glass transition temperatures (T_g) of these polymers are measured using a Differential Scanning Calorimeter (Perkin Elmer DSC-7) during the second heating run with a heating rate of 20 °C/min. Testing specimens of polymer blends that were approximately 20 mm long, 2 mm thick and 4 mm wide are prepared by compression moulding at 220 °C during 5 minutes. These specimens are investigated by dynamical thermal analysis (DMTA) (Polymer Laboratories, MKIII) in the tensile mode with a heating rate of 2 °C/min and a frequency of 1 Hz. Intrinsic viscosities are measured using SEC implementing a viscodetector (Viscotec Model 40), using THF (40 °C) as eluent, 3 APS linear columns and a flow rate of 1 ml/min.

Materials
Linear PS (N5000) is obtained from 'Bredase Polystyreen Maatschappij' (M_n=80000 g/mol, M_w=260000 g/mol). Linear PPE (PPO803) is obtained from General Electric Plastics (M_n= 14500 g/mol, M_w=30150 g/mol). Star-shaped PPEs were prepared as reported previously (15). Star polymers with 4,8,16,32, and 64 arms, depending on the generation of the poly(propylene imine) dendrimer core, are used with an estimated arm length of 90 PPE repeating units.

Preparation of PPE/PS blends
The 50/50 wt% PPE/PS blends were prepared using a laboratory-scale mini-extruder, which operates continuously or batchwise. The device consists of two co-rotating, closely intermeshing, self-wiping, conical screws and is equipped with a recurrent loop and valve system. The device allows processing small quantities of material (volume = 6 cm^3) at temperatures up to ~ 400 °C in a way equivalent to large-scale industrial co-rotating twin screw extruders. All 50/50 wt% star/linear and linear/linear blends were extruded at 230 °C, during 3 minutes.

Results and Discussion
Materials
The star-shaped PPEs are prepared by a redistribution reaction of PPE with a multifunctional phenol as previously described (15). This approach yields star polymers with a poly(propylene imine) dendrimer core and 4, 8, 16, 32, or 64 polymer arms depending on the dendrimer generation. For example, using DAB-*dendr*-(NH$_2$)$_{64}$, a modified dendrimer with 64 tyrosine endgroups (DAB-*dendr*-(NH-*t*-BOC-L-Tyr)$_{64}$ can be prepared. Redistribution of this N-*tert*-BOC-protected tyrosine modified dendrimer with 61.8 moles of PPE (M_n = 11.2 kg/mol) yields a 64-arm star-shaped PPE (Figure 2) with an estimated average arm length of 90 PPE repeating units.
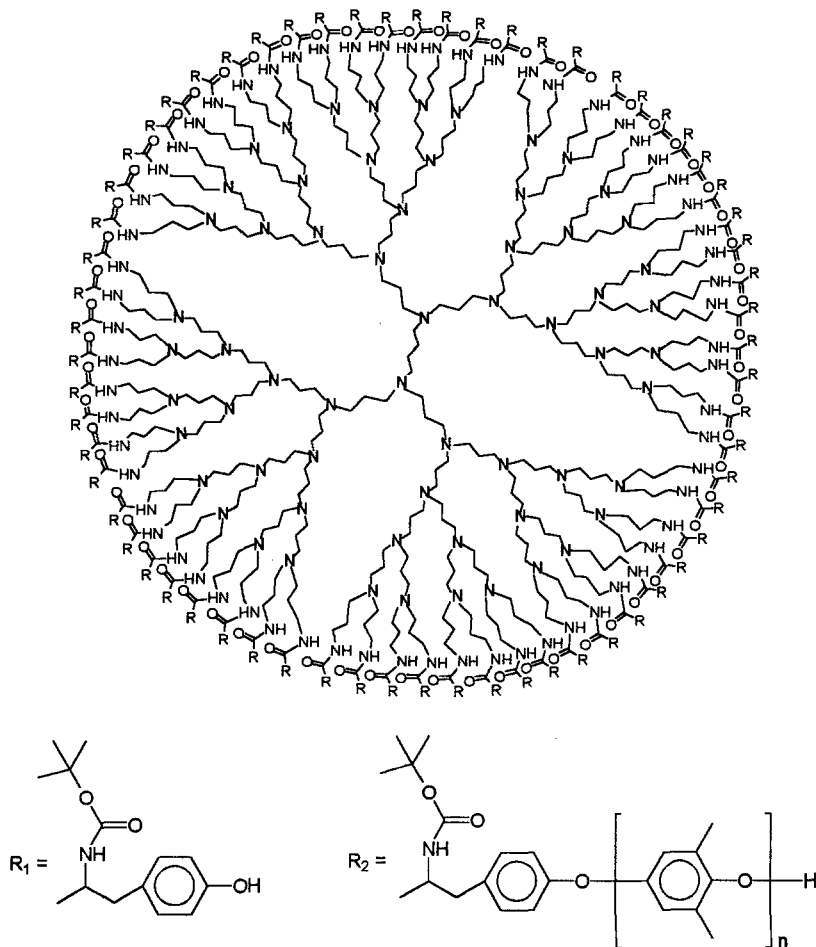
Figure 2: Dentritic structure using R = R$_1$: (DAB-*dendr*-(NH-*t*-BOC-L-Tyr)$_{64}$ and using R = R$_2$: 64-arm PPE star-shaped polymer prepared from (DAB-*dendr*-(NH-*t*-BOC-L-Tyr)$_{64}$

The number of phenolic endgroups can be varied by reacting the fifth-generation (64 end groups) amino-terminated poly(propylene imine) dendrimers with a mixture of tBoc-protected hydroxysuccinimide activated esters of L-tyrosine and D-phenylalanine. Employing these modified dendrimers in the PPE redistribution only the number of arms is varied but not the size of the dendritic core which is constant for each generation. Now that we can easily control the number of arms of the PPE star polymers, it is interesting to study its influence on physical behaviour in solution and in blends with PS.

Blends of star-shaped PPE and linear PS
Miscibility behaviour of blends is usually investigated by determination of glass transition temperatures. As a reference, we determined glass transition temperatures by

differential scanning calorimetry (DSC) of the star polymers, which are used in blends with linear polystyrene (PS). We observed an independence of core generation on the T_g of the star polymers by DSC and no large differences are observed in T_g of the star-shaped PPEs in comparison with a linear PPE (Table 1). This is in agreement with the theoretical treatment of the glass transition temperature (T_g) of dendritic polymers as described by Stutz (18). In star or dendritic polymers the glass temperature is dependent only on the molecular weight of a dendron, but not on the molecular weight of the whole molecule. Therefore T_g is governed primarily by the backbone glass temperature and depends little on grafting functionality. Only minor differences between linear macromolecule and dendritic structure are obtained, since the influences of endgroups and branching compensate each other to a large extent.

Table 1: Glass transition temperatures as measured by DSC, heating rate 20 °C /min, second heating run

polymer type	estimated number of arms	average arm length (repeating units)	T_g (°C)
linear PS	1	909	107.0
linear PPE	1	93	209.1
star PPE	4	90	210.4
star PPE	8	90	211.1
star PPE	16	90	209.8
star PPE	32	90	209.9
star PPE	64	90	211.2

Both star-branched PPEs and linear PPE are employed in blends with linear polystyrene at a 50/50 wt% ratio. Phase morphology is investigated by dynamic mechanical thermal analysis (DMTA). The homogeneous linear PPE - linear PS blend shows a single tan δ peak after extrusion as expected. When a 4-arm star polymer is extruded with linear polystyrene, a slightly broadened tan δ peak is observed (Figure 3A). Phase separation becomes more pronounced when the number of arms of the star-branched PPE is increased. The tan δ peak for the 8-arm star polymer is more broadened. Beyond 8 arms two tan δ peaks are observed, indicating that phase separation occurs (Figure 3B). The extruded samples clearly show that the liquid-liquid demixing enhances for higher number of arms of the star polymer. Extruded blends with 4- or 8-arm star-shaped PPE are transparent and show high toughness. Extruded blends with 32-or 64-arm star-shaped PPE are opaque and extremely brittle. Moreover, blends with highly branched PPE show severe delamination and are proposed to have the star polymer as continuous phase. The DMTA results are summarized in Table 2. The phase-separation of polystyrene and PPE star polymers becomes more pronounced at high number of arms, due to lower ability of the polystyrene chains to entangle with the PPE star polymer. By now studying the properties of the star polymers in solution, we can further elucidate their properties.
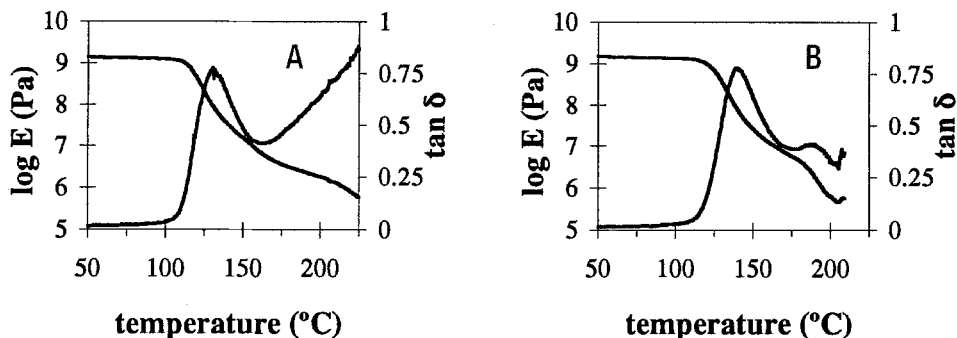
Figure 3:   A) DMTA scan blend 50 wt% 4 armed star PPE 50 wt% linear PS ;
             B) DMTA scan 50 wt% 64 armed star PPE / 50 wt% linear PS

Table 2: tan δ peaks as measured by DMTA;
[a] no clear tan δ peak, sample specimen breaks at 184 °C

blend type PS/PPE	first tan δ peak (°C)	second tan δ peak (°C)
linear/ linear	160.4	-
linear/ 4 star	132.2	-
linear/ 8 star	154.1	-
linear/ 16 star	139.0	173.6[a]
linear/ 32 star	128.7	166.9
linear/ 64 star	139.8	189.3

Star-shaped PPEs in solution

Previously, we studied some solution properties of the star polymers (15). We extended this investigation as a comparison to the miscibility study in blends. Our main interest is to see whether the less entangled and more dense packing of star polymers at high number of arms is also reflected in the solution properties.

Size Exclusion Chromatography (SEC) can be a powerful tool for characterization of star-branched polymers (19), especially when a Low-Angle Laser Light Scattering detector (LALLS) is implemented. However, in our case the star polymers gave too low scattering intensities to obtain reliable data from LALLS. As described previously (15), star-shaped PPEs with a same estimated arm length of 22.5 units with different dendritic core generation and therefore different number of arms, show the same hydrodynamic volume in SEC. The difference in core-size is not expressed in a hydrodynamic volume change. However, DLS shows a large deviation in measured hydrodynamic radius (R_H) of these star polymers. The R_H increases with the number of arms. This increase is proposed to be caused by a restricted mobility of the more densely packed PPE arms at higher number of arms. To investigate the influence of the varied core-size, we prepared star polymers with same core-size but different number of arms by partial modification with tyrosine endgroups. These model compounds are prepared from a fifth generation poly(propylene imine) dendrimer, modified with a mixture of tBOC-protected hydroxysuccinimide activated esters of L-tyrosine and D-phenylalanine. Only the tyrosine

endgroups will react with PPE in a redistribution. Using these star polymers, DLS and SEC measurements gave similar results as obtained with the star polymers prepared from different dendrimer generation. This confirms the compact structure of the star polymers with more densely packed polymer arms at high number of arms. This compact structure of star polymers is also reflected in the intrinsic viscosities, as measured with SEC implementing a visco-detector and refractive index (RI) detector. The measured intrinsic viscosities (IV) from this visco-detector decrease when the number of arms is increased, either by increasing the dendrimer generation or tyrosine/phenylalanine ratio (Table 3). These lower IVs are caused by less entangled and more dense packed PPE arms. This typical compact structure of star polymers will also affect their miscibility behaviour with linear polymers.

Table 3: Intrinsic viscosities in THF measured by SEC/viscometer

polymer type	dendrimer generation	tyrosine/ phenylalanine ratio	estimated number of arms	average arm length (PPE-units)	batch IV (dL/g)
linear	-	0/0	1	39	0.157
star	2	100/0	8	22.5	0.052
star	5	100/0	64	22.5	0.041
star	5	40/60	25.6	22.5	0.081

Conclusions
Star-shaped polymers with a high number of PPE arms give rise to inhomogeneous blends with linear polystyrene. The increase in the width of the damping peak (37) is caused by a decreased solubility of the star branched PPE in PS at high number of PPE arms. Presumably, the polystyrene chains are unable to interprenetrate and entangle with the densely packed PPE arms of this star polymer. The solution properties of the PPE stars are consistent with this miscibility behaviour. Star polymers with constant arm length but increasing number of arms show the same hydrodynamic volume as measured by SEC, but decreasing hydrodynamic radius as measured by DLS. This confirms the dense packing of the polymer arms of the star-shaped PPE. Intrinsic viscosities decrease at higher number of arms, caused by less entangled and more densely packed arms.

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