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Effect of the degree of branching on the glass transition temperature of polyesters

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ABSTRACT

Glass transition temperature dependence on the branching degree can be empirically estimated by excluding additional effects on this parameter as molecular weight distribution, end group interactions or crystallization. In this communication aliphatic–aromatic polyesters with a well defined degree of branching between 0% (linear) and 50% (hyperbranched) are investigated by differential scanning calorimetry. The hydrogen bonding effect of the OH-terminal groups was successfully extracted from the pure branching effect by protection of the end-functionalities. Fractionation of samples with variation of the branching degree and end-functionalities led to series of narrowly distributed molar masses. The dependence of the molecular weight on the glass transition temperature for different branching degrees was calculated and compared for polar and non-polar end groups.

1. Introduction

Hyperbranched (hb) polymers are functional materials, which can be easily prepared by "one pot" polymerization, which, in turn, is accompanied by reduced costs as compared to the dendrimers [1–3]. However, despite the fact that many hb structures were synthesized and comprehensively characterized, some uncertainties in their structure-property relations still exist. One of those is the relation between the branching and glass transition temperature, which is an essential parameter influencing the material properties.

To clarify this relation several investigations [2,4–6] on differently branched polymers were performed but no apparent correlation between the branching and the glass transition temperature was obtained. Moreover, the experimental observations showed two different tendencies. The first tendency states that the glass transition temperature of highly branched polymers only slightly depends on the branching. This conclusion is supported by results of Wooley et al. [7], where similar glass transition temperatures were found for the linear, hb and dendritic aromatic polyesters having identical repeating unit, as well as number and nature of functional groups. Similar observation was done by two other groups. Ramakrishnan et al. [8] compared the thermal behavior of linear, branched and "kinked" PET and indicated similar glass transition temperatures for all three types of architectures. Furthermore, Finelli et al. [9] reported on the comparison between the linear and branched poly(butylenes isophthalates), confirming the lack of the effect of branching on the glass transition temperature. However, it should be mentioned that the glass transition temperature behavior of those polyesters was additionally influenced by their partially crystalline nature where the crystallinity acts similarly to the crosslinking and causes a raise of the glass transition temperature through its restrictive effect on the segmental motion of the polymer chains.

The second tendency implies that the branching causes a decrease of the glass transition temperature. This trend was observed in hb polyetherimides [10], indicating a significantly enhanced segmental mobility with branching. A comparative study on hb and linear polyimides [11] showed, that the introduction of branching leads to glass transition temperature decrease from 266 °C for linear polyimide down to 222 °C for amino-terminated- and 231 °C for the anhydride-terminated hb polyimides.

Additionally, besides those described theories there is an interesting study made by Zhu and co-workers [4] on the amorphous poly[3-methyl-3-(hydroxymethyl)oxetane] revealing an increase of the glass transition temperature with branching, which passes through a maximum at DB = 27% and then decreases sharply. The branching leads actually to two main effects – restriction of the segmental mobility, which leads to increasing glass transition temperatures and simultaneous increase of end groups number and free volume respectively which decreases the T_g.

The observation of these controversial tendencies gave us motivation to search for the pure effect of branching on T_g minimizing overlapping effects. In the above mentioned studies the branching effect is accompanied by the effect of end group interactions [6], different amount of end groups per monomer unit

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[10,11] or crystalzation [4,9]. In order to extract the branching influence on T_g we focused on amorphous aromatic-aliphatic polyesters with hb, gradually branched and linear architecture and controlled amount of functional groups. These polymers are of identical chemical origin possessing two types of functional groups with different polarity. Additionally, fractionation was carried out in order to clarify the molar mass effect on T_g at different degree of branching.

2. Experimental section

2.1. Samples

The synthesis of the samples is described in a previous work and schematically shown in Scheme 1 [12]. The following sample abbreviation was used: OH- and SY- corresponds to the type of functional groups (OH = hydroxyl group and SY = t-butyldimethylsilyl group). The number indicates the degree of branching (DB) which is calculated to be 0 for linear and 50 for the hb samples.

2.2. Fractionation

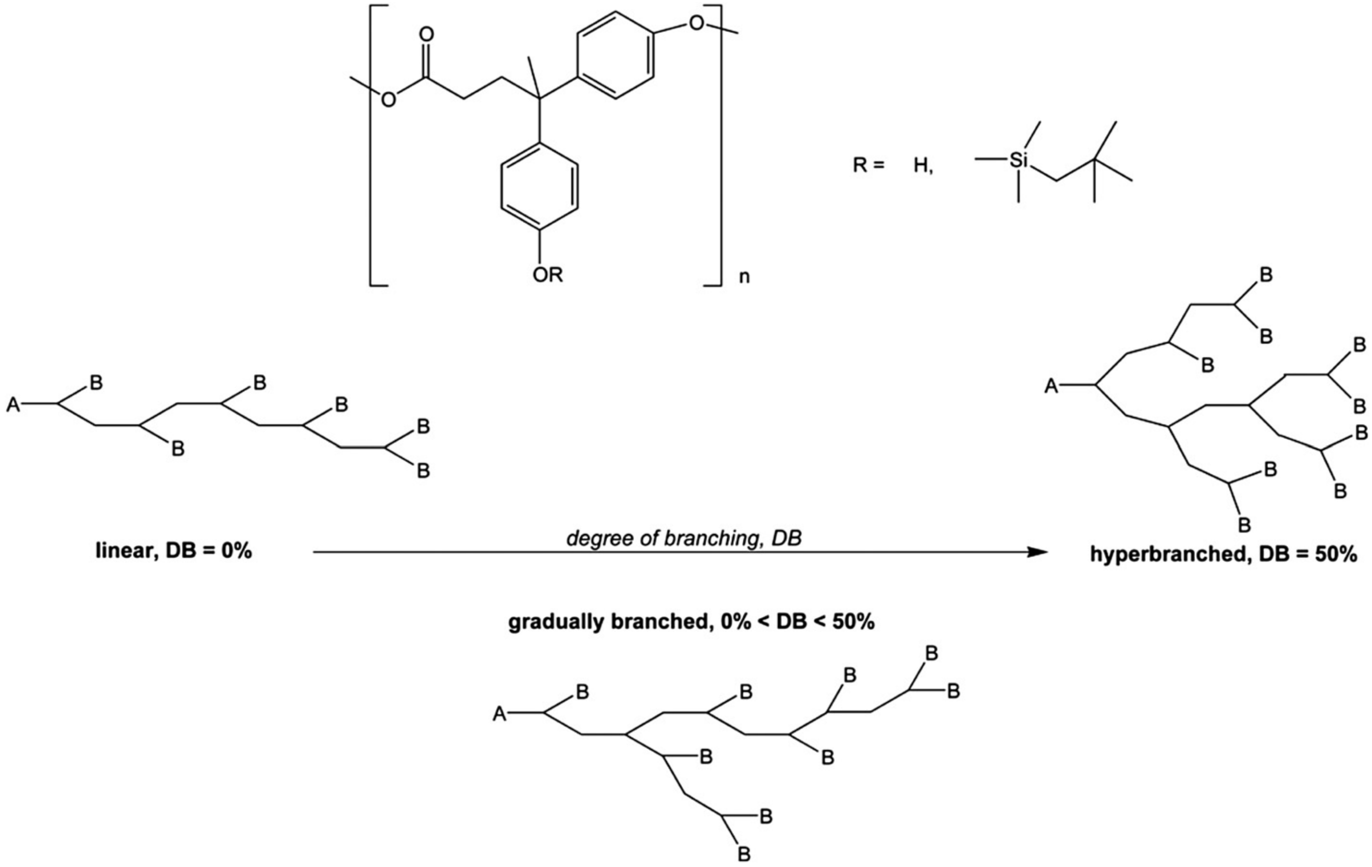
Fractions of narrow polydispersity were obtained using preparative elution fractionation similar to previously described procedures [13,14]. This separation technique is based on the selective extraction of the fractions according to their solubility in an eluent with gradient in the thermodynamic quality. The gradient depends on the eluent composition – different ratio of non-solvent to solvent (NS/S) compositions. Since two different types of the functional groups were used, two different NS/S systems were applied. OH-terminated hb samples were fractionated in n-hexane/tetrahydrofuran (THF) as an NS/S eluent system. For all SY-terminated samples methanol/acetone as NS/S system was used. All fractionations were performed at room temperature.

The supporting material Ballotini (glass beads, 0.1–0.2 mm diameter) was coated with the corresponding polymer (1.3–2.2 g) by evaporation of the polymer solution. The 100 cm high fractionation column was filled with the non-solvent and the coated glass beads. The NS/S gradient started at 0% up to 100% with a flow rate of approx. 2.5 mL/min. The fractions were collected in 250 mL flasks and the solvent was removed by evaporation. The fractions were dried under vacuum at 40 °C for at least 24 h for subsequent investigations.

2.3. Characterization

Determination of the molecular weights was performed by size exclusion chromatography (SEC) equipped with HPLC pump (Knauer, Germany) and coupled to a viscosity/differential refractive index (RI) dual detector (ETA-2020, WGE Dr. Bures, Germany) and a multi angle laser light scattering-detector (MALLS) Dawn®EOS (Wyatt Technologies, USA). A PLgel 5 μm Mixed C chromatography column 300 mm × 7.5 mm (Polymer Laboratories, Ltd., UK) was used with THF (Acros, Germany) as an eluent. Flow rate was 1 mL/min. All evaluations were made with the software ASTRA 4.9 (Wyatt Technology Corporation, USA).

Thermal gravimetric analysis (TGA) measurements were carried out with a TGA-Q5000 of TA Instruments in the temperature range 30–750 °C at a heating rate of 10 K/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were carried out with Q1000 of TA Instruments in the temperature interval from −60 to 200 °C under a nitrogen atmosphere.



Scheme 1. Well defined branching architectures based on the same AB_2 monomer. Variation either only in the degree of branching or only in functional groups type (R).