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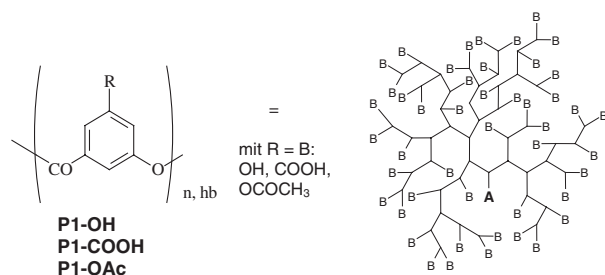
# Functional Hyper-Branched Polyesters for Application in Blends, Coatings, and Thin Films\*

By Brigitte Voit\*\*, Detlev Beyerlein, Klaus-Jochen Eichhorn, Karina Grundke, Dirk Schmaljohann, and Ton Loontjens

## 1 Introduction

Hyper-branched polymers (HBP) can be prepared in one-pot poly-reactions from  $AB_x$  monomers. Often, a classical poly-condensation type reaction, e.g., in the melt, based on  $AB_2$  monomers is employed. These monomers contain a functionality A, and a second functionality B where A and B can react only with the opposite functionality. The resulting highly branched but soluble polymers contain a large number of unreacted B functionalities. These polymers exhibit specific properties due to their globular, highly functional structure and are of significant interest due to their main potential applications in blends, coatings or resins, or as additives to linear polymers [1]. Also of interest are thin films of functional hyper-branched (hb) polymers similarly prepared on solid surfaces as has been shown for perfect dendrimers which may be useful as sensor materials or diagnostic tools.

Polyesters were one of the first hyper-branched materials studied [2] due to the relatively good availability of suitable  $AB_x$  monomers, e.g., Perstorp commercialized hyper-branched aliphatic polyesters under the trade name "Boltorn" for resin and coating application. A variety of fully aromatic, mixed aromatic-aliphatic, and pure aliphatic hyper-branched polyesters with different functional groups were prepared [3,4]. In Fig. 1 the representative average linear repeating unit is given for an aromatic hyper-branched polyester with the schematic branched structure as it results from the condensation of a  $AB_2$  monomer.



**Figure 1.** Schematic representation of a hyper-branched polymer and the simplified chemical structure for aromatic hyper-branched polyesters **P1**, given as linear repeating unit.

[\*] This work was presented as a lecture at ECCE 2001 in July 2001 in Nürnberg, Germany.

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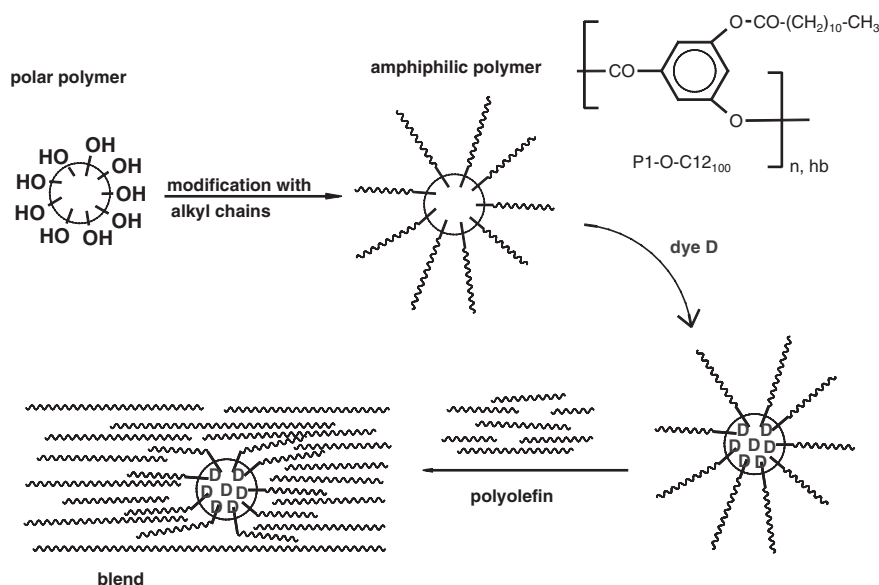
When only one B functionality of the  $AB_2$  monomer reacts (e.g., acid group or phenol group) it results in the linear unit shown, reaction of both B functions leads to a so-called dendritic (branched) unit and in the case where no B function reacts, a terminal structural unit is obtained.

## 2 Hyper-Branched Polyesters in Blends and as Additives

Hyper-branched polymers were reported as being mixed with commercial linear polymers as early as 1990 by Kim and Webster [5]. Enhanced miscibility would be expected from these hyper-branched materials with linear polymers and additional positive effects on the mechanical, thermal and rheological properties of the mixture. Hyper-branched polyesters are miscible on a molecular level with several linear polyesters and polyamides [6]. However, due to missing entanglements, hyper-branched polymers are more brittle than their linear analogs and subsequently, in a blend with linear polymers they reduce toughness, even though the modulus might be improved, e.g., as observed for a blend of hb polyesters with linear polycarbonate [6].

Hyper-branched polymers are used as additives in order to optimize melt rheology of a linear thermoplastic or to enhance compatibility between two blend components, between a matrix and a filler, and between a nonpolar matrix polymer and a polar additive. For the use of relatively polar hyper-branched polyesters in polyolefins, for example, it is advisable to modify the polar end groups of the hb component using nonpolar long alkyl chains. The product of the complete modification of the aromatic hyper-branched polyester **P1** (compare Fig. 1 and Fig. 2) with a fatty acid is an amphiphilic polymer (**P1-O-C12<sub>100</sub>**) which differs strongly in its solubility, thermal and mechanical properties from the polar starting material [7].

With the help of these amphiphilic hyperbranched products, which can be compared with unimolecular micelles (polar interior, nonpolar "shell"), it is possible to carry, disperse and stabilize polar additives (e.g., dyes, stabilizers, processing aids) in a nonpolar matrix polymer. Today it is still a problem to dye nonpolar polypropylene fibers with organic dyes since the dye is not soluble in the matrix material and thus it crystallizes leading to inhomogeneous color distribution or it diffuses to the surface (bleeding). In Fig. 2 the effect of an amphiphilic hb polymer as a "carrier molecule" for such polar dye molecules is shown schematically. The amphiphilic polymer is dissolved together with the dye, the polar dye diffuses into the polar interior of the hb molecule where it can interact, e.g., via hydrogen bonding and is stabilized against the surrounding by the nonpolar alkyl chains. After precipitation of the polymer and intensive washing to remove non-absorbed dye, most of the dye stays physically attached inside the hb molecule and can be finely dispersed together with the hb carrier molecules in a polyolefin matrix by compounding [8,9].



**Figure 2.** Schematic representation of the incorporation of dye molecules in an amphiphilic hyper-branched polyester (containing long alkyl chain end groups, **P1-O-C12<sub>100</sub>**) and the subsequent melt mixing with a nonpolar matrix polymer (e.g., polyolefin).

Using this principle it was shown that it is possible to disperse a blue organic dye homogeneously in a polyolefin matrix. In total 5 wt. % of the hb polyester/dye mixture was added to the polyolefin. After compounding the dye could not be removed from the matrix polymer by means of extraction with boiling water or soap solution. The crystallization behavior and the mechanical properties of the polyolefin (PE or PP) remained almost unchanged compared to pure polyolefin. In addition, the processing was somewhat improved since the hb additive showed a so-called lubricant effect [8,10].

It should be noted that in this case no homogenous blend was achieved between the polyolefin and the hb polyester. However, the modification with alkyl chains strongly affects compatibility, thus the domains of the hb polymer, which carry the dye, are very small in the range of 150–500 nm, even when 10–20 wt.-% hb polymer is added to the polyolefin. In general the compatibility effect is more pronounced in polyethylene compared to polypropylene. However, in both matrix polymers the dyeing was homogenous to the naked eye.

### 3 Hyper-Branched Polyesters in Coating Applications

The high functionality combined with the low solution viscosity of hyper-branched polymers led to early attention for the application of these materials in coatings as a multifunctional cross-linker [11]. Of particular interest are high solid formulations, which contain no, or only a very small amount of solvent as well as alternatives to acrylate systems in

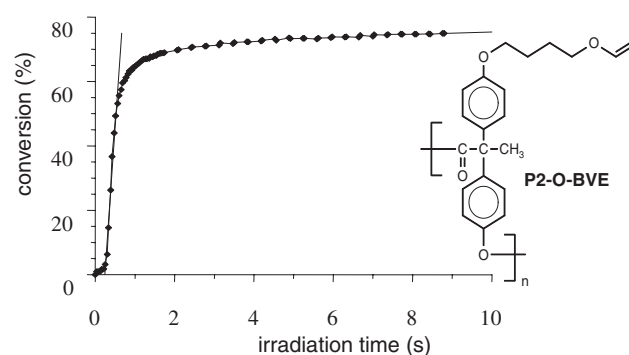
UV cured resins. A hyper-branched polyester was modified, it was based on 4,4-bis(4'-hydroxyphenyl)pentanoic acid, with vinyl ether and oxetane functional groups (**P2-O-BVE**, compare Fig. 3, and **P2-Ox**) [12] for application in UV curable coatings using cationic photoinitiators (photo acid generators).

The cationically crosslinkable groups should substitute the common radically cured acrylate groups.

The aliphatic-aromatic hyper-branched polyester **P2-OH** was chosen as the material for coatings due to the availability of a suitable AB<sub>2</sub> monomer and the good stability of the polyester towards acid and base. The degree of modification of the OH groups with vinyl ether or oxetane groups was varied between 30 and 80 % in order to optimize the coating compositions.

The modified polymer, **P2-O-BVE**, was mixed with a reactive diluent (triethylene glycol divinylether) and an UV initiator (photo acid generator based on a sulfonium salt), and films were coated onto aluminum substrates. Upon UV irradiation a very fast (few seconds) and nearly complete reaction of the vinyl groups was observed by in-situ FT-IR rapid scan analysis (Fig. 3).

The coatings showed sufficient crosslinking and mechanical stability in coating tests when a 50/50 mixture of the **P2-O-BVE** with the reactive diluent was applied. Without a diluent, only incomplete reaction (max. 30 % conversion) of the vinyl ether groups was observed due to the very fast reduction in mobility of the reactive groups in the highly crosslinked layer. The presence of some unmodified phenol groups in the polymer did not disturb the crosslinking reaction in the vinyl ether products. The oxetane modified products, however, reacted very slowly in all attempts at crosslinking.



**Figure 3.** Conversion of the vinyl ether groups in the coating upon UV-irradiation; conversion was determined by rapid scan in-line FT-IR spectroscopy (system: **P2-O-BVE**/triethyleneglycol divinylether 1:1, 2 % UV initiator).

## 4 Surface Properties and Swelling Behavior of HBP

Recently, branched polymers based on acrylic acid and acrylamide were grafted from surfaces and studied as sensor materials [13]. The branched structure in combination with a high number of functional groups in a confined environment seem to favor the ability to adsorb selectively volatile organic compounds (VOC's). In contrast to these surface grafted polymers hyper-branched polyesters coated simply onto a substrate were studied [14].

From fully aromatic hyper-branched polyesters (**P1**) having hydroxyl, carboxyl and acetoxy end groups (compare Fig. 1, Tab. 1) thin layers of 80–90 nm thickness were prepared by spin-coating on silicon wafers or glass substrates in order to obtain an insight into their surface properties.

Isotropic thin films of HBP with a smooth surface were obtained. These films were studied extensively using AFM, ATR-FT-IR, zeta potential and contact angle measurements, and ellipsometry [14].

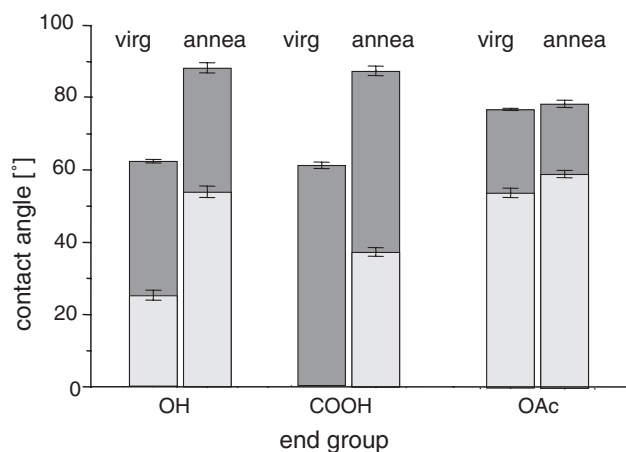
The zeta potential as well as the contact angle measurements revealed the presence of hydrophilic, acidic groups at the surface for **P1-COOH** and **P1-OH** films. When these films were annealed above  $T_g$  the surface free energy decreased drastically due to the rearrangement of the surface groups into the bulk phase of the film. This can be seen clearly by the increase in the contact angles (see Fig. 4) and by the shifts in the isoelectric point in zeta potential measurements after annealing.

**P1-OAc** surfaces are less hydrophilic and these do not change their surface properties after annealing.

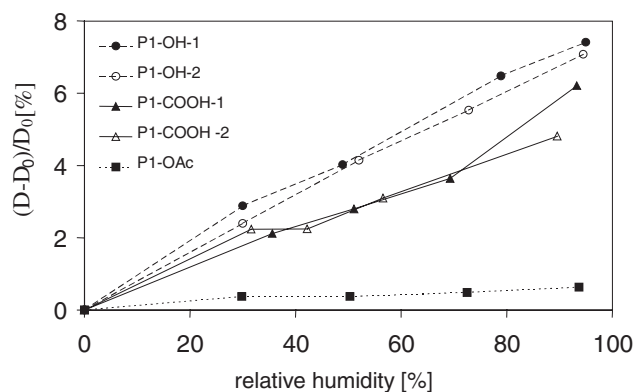
The differences in molecular structure and surface properties of these three types of hb polyesters result in differences in the swelling behavior under atmospheric humidity. The hydrophilic HBPs show a strong effect in contrast to the less hydrophilic **P1-OAc**. This behavior has been studied by in-situ ellipsometry in an atmosphere with defined amounts of humidity (Fig. 5).

The relative increase in thickness of the films correlates linearly to the relative humidity of the atmosphere. The fitted refractive index versus the relative humidity should also display a linear relationship, but the changes are very small and within the error of the fitting process. Only for the highest measured relative humidity a trend to lower refractive index values is detectable.

The difference between the hydrophilic and the more hydrophobic polymers is quite obvious: the hydroxyl- and the



**Figure 4.** Contact angle measurements on **P1-OH**, **P1-COOH**, and **P1-OAc**, measured on the virgin (virg) film and after annealing (annea.) above  $T_g$  (1 h at 180 and 240 °C, resp.); dark: advancing angle, bright: receding angle.



**Figure 5.** Increase in film thickness of hyper-branched polyesters **P1** (different end groups) dependent on the relative atmospheric humidity ( $D_0$  = original film thickness,  $D$  = equilibrated film thickness after swelling; several samples have been measured by in-situ ellipsometry).

carboxylic acid-terminated materials show an increase in thickness of about 7 % while **P1-OAc** swells only about 0.5 %. For verification, different samples of the same material were exposed statistically to different humidities and the same values of swelling were detected (Fig. 5). In comparison to other aromatic polymers applied as sensoric layers like aromatic polyimides, the swelling of the polar hb polyesters is very strong [15] whereas polyelectrolytes covalently bound to the surface show, as expected, a stronger effect [16] but a totally different mechanical behavior.

Independent measurements of relative changes in the optical thickness ( $nD$ ) performed by Reflectometric Interference Spectroscopy (RIfS) confirmed the ellipsometric data and demonstrated the reversibility of the water adsorption/desorption processes. The increase in film thickness is quite rapid and the final value was reached in a few minutes. Also, it takes just a few minutes to drop to the starting value when the humidity has

**Table 1.** Properties of aromatic hyper-branched polyesters (**P1**).

End group R	Sample	$M_w$ [g/mol]	$T_g$ [°C]	Degree of branching DB <sup>1</sup>	Water Content [%]
-OH	<b>P1-OH</b>	16,000	220	0.60	1.9
-COOH	<b>P1-COOH</b>	15,500	235	0.50	2.1
-OCOCH <sub>3</sub>	<b>P1-OAc</b>	13,500	155	0.50	0.3

<sup>1</sup> DB = D+T/L+D+T (L, D, T = different structural units, linear L, dendritic D, terminal T)

been reduced to zero. Several cycles have been measured and in all cases the original values have been restored.

In the preliminary tests which have been carried out in cooperation with the group of Prof. Gauglitz at the University Tübingen, the adhesion to the substrate of the simple spin-coated films has been sufficient to allow repeated measurements over several hours. However, for technical applications the use of an adhesion promoter is recommended. It should be kept in mind that the hyper-branched polymers are not crosslinked and therefore fully soluble, e.g., in polar solvents that might cause problems in long-term tests. Nevertheless, beside the sensitivity of these functional polymer layers towards humidity, several alcohols, fluorinated compounds, and some gases were also tested successfully. Again, different sensitivities and therefore specific selectivity could be observed for hb polymer samples having different end groups.

From these results it was concluded that hyper-branched polymers with different end groups swell selectively in volatile organic compounds (VOC) with different polarity. Thus, this kind of HBP film seems to be an interesting material for chemical sensors.

## 5 Conclusions

Hyper-branched polyesters with different functionalities and different mechanical properties can be synthesized in a conventional melt polycondensation from various AB<sub>2</sub> monomers. By suitable modification it is possible to optimize these materials for application as additives, in blends, for coatings or as sensor material. The high functionality in a constrained molecular geometry, high solubility, low solution viscosity, interesting melt rheology as well as the branched and thus globular structure allow an improved property profile compared to linear polymers.

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## Video Microscopy for the Examination of the Heterogeneous Gas-Phase Polymerization

By *Knut Zöllner and Karl-Heinz Reichert\**

### 1 Introduction

Catalysts are characterized on the laboratory scale for process design and catalyst development using autoclave sizes of 1 to 5 liters. Two different techniques are applied to polymerizations in gas-phase reactors. Either the overall activity of the catalyst is measured in a stirred bed reactor, or investigations on the scale of single catalyst particles are carried out. In this case single particles are separated from the polymerization and they are characterized, e.g., by scanning electron microscopy (SEM), or by transmission electron microscopy (TEM) [1–3]. Unfortunately information about the activity of single particles is not possible with these techniques.

The combination of a small reactor and a microscope to observe the gas-phase polymerization of heterogeneous catalysts was first published by Eberstein [4]. Using this technique, kinetic studies of single resting polymerizing particles are possible. The quality of the results is strongly influenced by the reproducibility of the experimental investigations and therefore an independent measurement system has to be used.

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