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*Published in:*  
Macromolecular Chemistry and Physics

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
2000

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### *Citation for published version (APA):*

Schmaljohann, D., Häußler, L., Pötschke, P., Voit, B. I., & Loontjens, T. J. A. (2000). Modification with alkyl chains and the influence on thermal and mechanical properties of aromatic hyperbranched polyesters. *Macromolecular Chemistry and Physics*, 201(1), 49-57.

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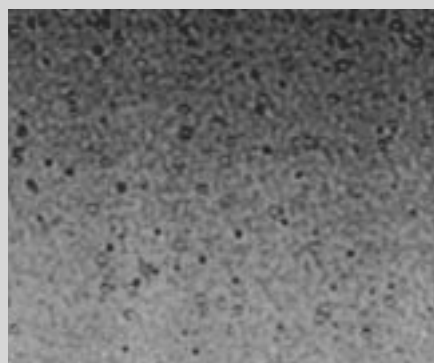
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All-aromatic hyperbranched polyesters with hydroxy end-groups were functionalized with aliphatic *n*-alkyl carboxylic acids. The length of the *n*-alkyl chain as well as the degree of modification were varied and the resulting, partially amphiphilic polymers were characterized by differential scanning calorimetry (DSC). With both increasing degree of modification and increasing length of the alkyl chain the glass transition temperature decreases due to reduced intermolecular hydrogen bonding. When the alkyl chains start to crystallize  $T_g$  of the hyperbranched polymers increases again. The mechanical properties of the former brittle hyperbranched polyester were improved by modification with C12 chains and a stable free standing film was obtained by compression molding. The film was investigated by means of dynamic mechanic analysis (DMA) and microscopy, exhibiting a low temperature thermal transition and phase separation within the scale of a light microscope. Furthermore melt rheology measurements were performed on the starting polymer and on the C12 modified product. The complex viscosity is reduced strongly by the modification of the aromatic hyperbranched polyester.



Light microscopy of P1b-O-C12<sub>98</sub> at 200 °C (310 fold magnification)

## Modification with alkyl chains and the influence on thermal and mechanical properties of aromatic hyperbranched polyesters

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(Received: January 8, 1999; revised: May 5, 1999)

### Introduction

The interest in hyperbranched polymers expanded strongly within the last years and the number of described structures is still growing<sup>1</sup>. Especially hyperbranched polyesters gained high interest due to good availability or easy synthesis of suitable monomers, and the readily realized one-pot polycondensation reaction<sup>2</sup>. One possible application of hyperbranched polyesters is their use in coating systems due to their low melt and solution viscosities, the large number of functional endgroups and thus, the possibility to introduce other functionalities by end-group modification<sup>3</sup>. However, the lack of entanglements in these products results in a brittle material. Therefore, the polymers need to be modified to improve the mechanical properties. A reduction of the  $T_g$  and higher flexibil-

ity can be achieved by modification of the hyperbranched polyester with alkyl chains<sup>3</sup>.

The glass transition temperature of a dendritic polymer is not only affected by the chain-end composition, but also by the molar mass and the macromolecular composition<sup>4</sup>. Here, the chain-end free volume theory has to be modified due to the large number of endgroups. It can be understood as a combination of inter- and intramolecular effects. Differences in  $T_g$  of hyperbranched polymers with different repeating units but equal endgroups demonstrate the intramolecular effect of segmental motion, whereas the influence of the  $T_g$  through variation of the endgroups can be assigned to translational motion and an intermolecular effect<sup>1,4,5</sup>. This intermolecular effect is strongly dependent on the polarity of the chain-end functionalities.

The alkyl modification of hyperbranched polyesters has been investigated first by Hult et al.<sup>6)</sup> with an aliphatic hyperbranched polyester based on 2,2-bis(hydroxymethyl)propionic acid. The very flexible all-aliphatic system shows a decrease of the glass transition temperature ( $T_g$ ) upon modification. The reduction of the  $T_g$  can be described as a result of reduced intermolecular hydrogen bonding since the hydroxy functionalities were capped by aliphatic chains. However, due to the very flexible polymer backbone the long alkyl chains tend to crystallize and again, an increase of the  $T_g$  of the polyester backbone is observed.

Now we present results on the modification of an aromatic hyperbranched polyester based on 3,5-dihydroxy benzoic acid<sup>7,8)</sup>. The modification was carried out with acyl chlorides of different chain lengths and also the degree of modification has been varied. The goal of this study is the improvement of the mechanical properties and the investigation of the effect of the modification on the  $T_g$ . Furthermore, the side chain crystallization and its influence on the glass transition temperature of the hyperbranched polymers are of interest. In contrast to the studies of Hult<sup>6)</sup>, we chose the rigid all-aromatic hyperbranched polyester which should exhibit a lower tendency to side chain crystallization.

## Results and discussion

### Polymer synthesis

The starting polymer was synthesized from 3,5-bis(trimethylsiloxy)benzoyl chloride in a melt polycondensation according to the literature<sup>7,8)</sup> (Scheme 1). Two products with different molar masses (**P1a-OH**:  $\bar{M}_n = 29700$  g/mol and **P1b-OH**:  $\bar{M}_n = 58900$  g/mol) were used in this study. Each polymer was the starting product in one series of modifica-

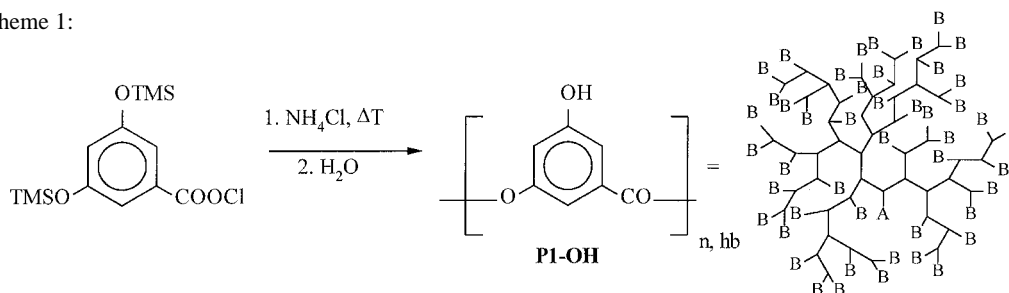
tion reactions, either the variation of the chain length of the modification reagent or the variation of the degree of modification ( $DM$ ). The molar masses and the  $T_g$  of the two starting polymers **P1a-OH** and **P1b-OH** are given in Tab. 1 and Tab. 2. The determination of the molar mass was carried out with size exclusion chromatography (SEC) in tetrahydrofuran (THF) as solvent and with a linear polystyrene calibration. The starting polymers had to be silylated for SEC analysis in order to avoid adsorption and aggregation effects. Since highly branched polymers have a more dense structure compared to the linear polystyrene the retention times will be longer and no realistic values will be achieved for molar masses. However, the results from SEC are useful for a comparison of the starting polymers with the modified products. More reliable values for molar masses could be obtained only for lower molar mass products ( $\bar{M}_n < 5000$  g/mol) using vapor pressure osmometry or NMR analysis.

### Modification reactions

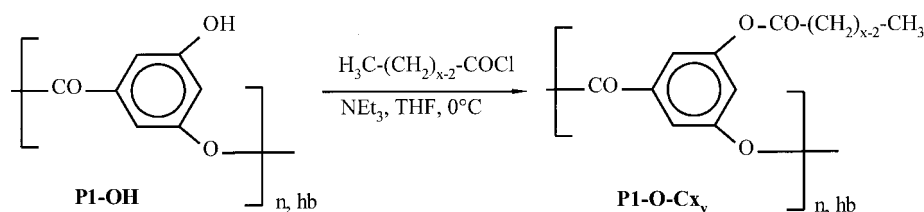
The hyperbranched polyester has a large number of phenol endgroups ( $n + 1$ ,  $n$  = number of repeating units) which can be easily functionalized<sup>2,3,6)</sup>. The functionalization with  $n$ -alkyl chains was achieved via esterification at low temperature with the corresponding acyl chloride in dry THF in the presence of an equivalent amount of triethylamine to trap the forming hydrochloric acid (Scheme 2).

The degree of modification can be calculated by <sup>1</sup>H NMR (Fig. 1) comparing the signal intensities of not fully modified structural units and fully modified structural units (compare Fig. 1 and Scheme 3). By analyzing the methylene group in  $\alpha$ -position it can also be distinguished between unreacted acid and the formed ester which is a control of the purity of the product (Fig. 1). Purification of the modified polymers, especially when long-chain fatty acids have been used, is often difficult due to the amphiphilicity of the products. When purification by precipitation was not possible due to the formation of colloidal suspensions, centrifugation was used to isolate the product.

Scheme 1:



Scheme 2:





Tab. 1. Modification results of **P1a-OH**; dependence on the chain length

Polymer	Modification reagent	DM in %	Content of acyl groups <sup>a)</sup> in wt.-%	$\overline{M}_n(\text{SEC})^{\text{b)}$ g/mol	$\overline{M}_w(\text{SEC})$ g/mol	$T_g^{\text{c)}$ °C	$T_m^{\text{c)}$ °C
<b>P1a-OH</b>	–	–	–	29 700	45 700	220	–
<b>P1a-O-C2<sub>96</sub></b>	C <sub>1</sub> H <sub>3</sub> COCl	96	24	33 100	61 700	162	–
<b>P1a-O-C4<sub>61</sub></b>	C <sub>3</sub> H <sub>7</sub> COCl	61	24	18 600	70 900	155	–
<b>P1a-O-C6<sub>80</sub></b>	C <sub>5</sub> H <sub>11</sub> COCl	80	37	13 700	49 900	53	–
<b>P1a-O-C8<sub>81</sub></b>	C <sub>7</sub> H <sub>15</sub> COCl	81	43	50 500	105 000	85	–
<b>P1a-O-C12<sub>100</sub></b>	C <sub>11</sub> H <sub>23</sub> COCl	100	58	48 200	109 000	–48 <sup>d)</sup>	–
						+34	
<b>P1a-O-C14<sub>62</sub></b>	C <sub>13</sub> H <sub>27</sub> COCl	62	49	29 200	73 900	90	<–30 <sup>e)</sup>
<b>P1a-O-C16<sub>98</sub></b>	C <sub>15</sub> H <sub>31</sub> COCl	98	63	47 300	121 000	61	–6
<b>P1a-O-C18<sub>56</sub></b>	C <sub>17</sub> H <sub>35</sub> COCl	56	52.5	49 000	127 000	119	–1

a) Relative weight of acyl groups in the polymer, calculated from the degree of modification.

b) Molar masses determined by SEC in THF, linear polystyrene standards; values can only be used for comparison of the samples.

c) DSC measurements, heating rate 20 K/min, 2nd heating.

d)  $T_g$  from DMA measurement,  $E''$  maximum (compare Fig. 6).

e) Melting endotherm too close to the beginning of the DSC measurement (–60 °C) to allow realistic evaluation.

Tab. 2. Modification results of **P1b-OH**; dependence on the degree of modification

Polymer	Modification reagent	DM in %	Content of acyl groups <sup>a)</sup> in wt.-%	$\overline{M}_n(\text{SEC})^{\text{b)}$ g/mol	$\overline{M}_w(\text{SEC})$ g/mol	$T_g^{\text{c)}$ °C	$T_m^{\text{c)}$ °C
<b>P1b-OH</b>	–	–	–	58 900	84 800	218	–
<b>P1b-O-C12<sub>16</sub></b>	C <sub>11</sub> H <sub>23</sub> COCl	16	18	28 500	65 300	160	–
<b>P1b-O-C12<sub>52</sub></b>	C <sub>11</sub> H <sub>23</sub> COCl	52	41	24 800	55 400	86	–
<b>P1b-O-C12<sub>99</sub></b>	C <sub>11</sub> H <sub>23</sub> COCl	99	57	34 400	81 500	–50 <sup>d)</sup>	–
						+52	
<b>P1b-O-C16<sub>11</sub></b>	C <sub>15</sub> H <sub>31</sub> COCl	11	16	17 200	33 100	180	–
<b>P1b-O-C16<sub>43</sub></b>	C <sub>15</sub> H <sub>31</sub> COCl	43	43	16 500	45 500	109	–11
<b>P1b-O-C16<sub>81</sub></b>	C <sub>15</sub> H <sub>31</sub> COCl	81	59	20 600	37 600	69	–8

a) Relative weight of acyl groups in the polymer, calculated from the degree of modification.

b) Molar masses determined by SEC in THF, linear polystyrene standards; values can only be used for comparison of the samples.

c) DSC measurements, heating rate 20 K/min, 2nd heating.

d) From low temperature DSC measurement; measurement started at –100 °C.

lapping effects like change in the solubility of the polymer and the accessibility of the functionalities as well as different reactivities of the reagents.

The variation of the degree of modification was studied only with the C12 and the C16 acyl chloride and leads to results, which are listed in Tab. 2. In these reactions the DM could be well controlled by the stoichiometry of the reagents.

The growing amphiphilicity and the lowering of the density by the introduction of long alkyl chains will change the hydrodynamic volume of the product. Therefore, the results of the SEC measurements for unmodified and modified polyesters cannot be compared accurately. Unfortunately, other methods like vapor pressure osmometry, analytical ultracentrifuge, or light scattering could not be applied successfully for these products due to the strong differences in polarity and solubility of the polymers. In some cases lower molar mass values compared to the starting product have

been observed by SEC after the modification, which indicates that certain polymer degradation has occurred during the reaction. Due to the presence of triethylamine, a base to trap the formed hydrochloric acid, water had to be excluded completely during the modification reaction in order to avoid the hydrolysis of the polyester backbone. We found that the hyperbranched polyester **P1-OH** is able to take up 12.5 wt.-% water just from air moisture. The presence of the water and triethylamine leads to significant degradation of the polymer backbone at room temperature in a few hours<sup>9)</sup>, however, with no change in the degree of branching as verified by NMR analysis. Although all polymers had been well dried before use, some samples may have contained a certain amount of water, which caused the degradation. Nevertheless, in all cases the molar mass of the products is high enough to neglect the influence of different molar masses on the thermal properties.

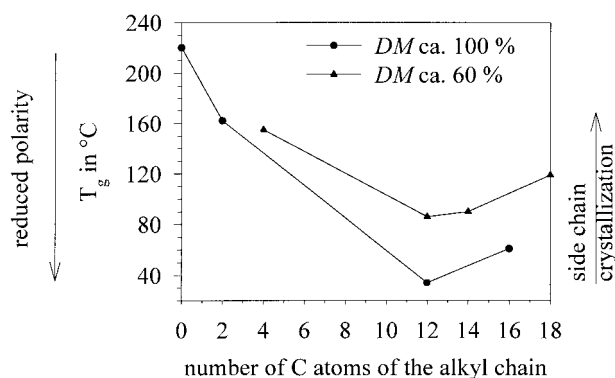


Fig. 2.  $T_g$  in dependence on the chain length and the degree of modification

### Thermal properties

It is known for hyperbranched polyesters that the transition from the polar hydroxy function to non-polar aliphatic endgroups yields in a strong decrease of the  $T_g$  because the intermolecular interaction of the polymer molecules are reduced<sup>2,3,10,11</sup>. By modification with fatty acids, the polar hydrogen bonding interactions are replaced by non-polar hydrophobic interactions. Furthermore, with increasing chain length and an increasing degree of modification, partial crystallization of the alkyl side chains is expected.

In our study we have to be careful to compare only products with nearly equal degree of modification for the discussion of the thermal properties. The comparison of **P1a-OH** with the product modified with C2 ( $DM = 96\%$ ) and C12 ( $DM = 100\%$ ) shows that the alkyl modification decreases the  $T_g$  with increasing chain length. But extending the chain length to C16 ( $DM = 98\%$ ) results in two effects: first, the side chains crystallize, second, the  $T_g$  rises again compared to **P1a-C12**.

The same effect can be observed for the samples with 60% modification: C4, C14, C18 (Tab. 1). Going from C4 to C12 (compare sample **P1b-O-C12<sub>52</sub>** from series 2, Tab. 2) a decrease in the  $T_g$  can be observed whereas for C14 and C18 crystallization occurs and again the glass transition temperature increases. In the case of C14 the melting endotherm could not be recorded completely in the temperature range of the DSC experiment.

A plot of the  $T_g$  versus the chain length (Fig. 2) indicates that a higher  $DM$  yields in a stronger decrease of the  $T_g$  with a minimum at C12. For better understanding the C12 sample from series 2 (Tab. 2) with 52% modification has been included in Fig. 2.

The alkyl modification of hyperbranched polyesters has also been investigated by Hult et al.<sup>6</sup> with a hyperbranched polyester based on 2,2-bis(hydroxymethyl)propionic acid. The very flexible all-aliphatic system shows similar results in the decrease of the  $T_g$  but a more pro-

Scheme 4:

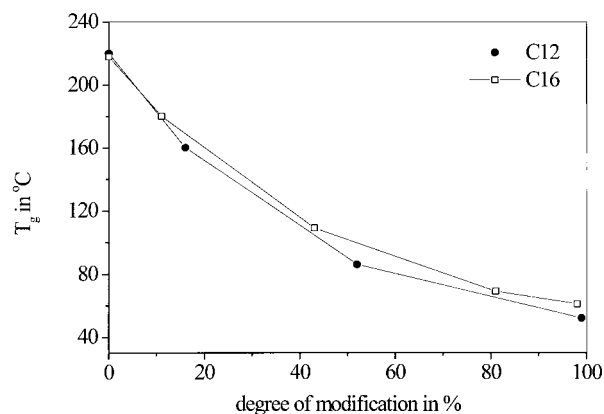
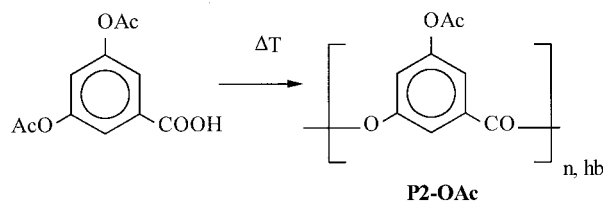


Fig. 3.  $T_g$  of **P1-O-C12** and **P1-O-C16** in dependence on the degree of modification

nounced tendency to side chain crystallization. This hyperbranched polyester has its  $T_g$  minimum at a modification with C6 chains, whereas the rigid aromatic hyperbranched polyester has its minimum at C12. This statement is also valid when not only the chain length but also the wt.-% of acyl groups in the modified polyesters are taken into consideration (compare Tab. 1 and 2).

The reduction of the  $T_g$  is caused by reduced hydrogen bonding capability. Therefore, the intermolecular interaction is lower and the mobility is increased. When the alkyl chains are long enough they can aggregate and crystallize. This crystallization causes an intramolecular phase separation and therefore, the effect of the  $T_g$  reduction is diminished. The overall effect is an increase in the  $T_g$  compared to fully amorphous modified samples, accompanied by the appearance of a melting endotherm in the DSC.

The C2 modification of **P1-OH** (**P1a-O-C2<sub>96</sub>**) leads to a glass transition temperature (162 °C) which is very similar to that observed for a polymer obtained by melt polycondensation of 3,5-bis(acetoxy)benzoic acid (**P2-OAc**) (Scheme 4) with a  $T_g = 155$  °C<sup>11</sup>.

The difference of 7 K in the glass transition temperature between **P1a-O-C2<sub>96</sub>** and **P2-OAc** can be explained as an effect of a small difference in the degree of modification (96% and 100%). Differences in the degree of branching (62% for **P1a-O-C2<sub>96</sub>** compared to 50% for **P2-OAc**<sup>11</sup>) as determined by NMR should not influence the  $T_g$  as Fréchet et al. have shown<sup>12</sup>.

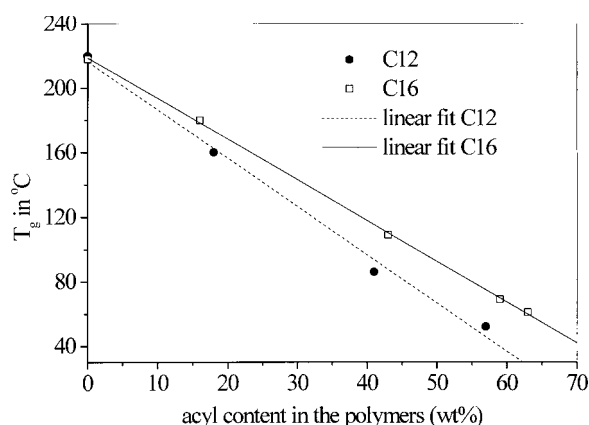


Fig. 4.  $T_g$  of **P1-O-C12** and **P1-O-C16** in dependence on the weight percent of acyl groups in the polymers (calculated from the degree of modification)

The increase of *DM* leads to a similar effect than enlarging the chain length (2): an increasing degree of modification causes a reduction of the  $T_g$  in the C12 and C16 modified samples with the glass transition temperature step becoming very weak for high side chain crystallization. The dependence of the  $T_g$  on the degree of modification (Fig. 3) is similar for both, C12- and C16-modification. However, when the  $T_g$  is plotted versus the wt-% acyl groups in the polymers a linear dependence for the C12 and the C16 samples can be observed (Fig. 4) with a lower slope for C16 ( $y = 218.8 - 2.52x$ ) compared to C12 ( $y = 216.2 - 2.99x$ ) in the linear regression. An explanation for this unexpected effect might be that the higher tendency to side chain crystallization of the C16 modified products leads to a weaker effect of the acyl content on the  $T_g$  of the samples. It should be mentioned also that a partial modification leads to an increased heterogeneity in the polymers: not only chains of different chain length and isomers with different branching distribution but also molecules with differences in the degree of modification have to be considered. This behavior has been studied recently in detail by Froehling et al.<sup>13)</sup> for partially modified poly(propyleneimine) dendrimers.

The samples nearly 100% modified with C12 (**P1a-O-C12<sub>100</sub>** and **P1b-O-C12<sub>99</sub>**) show beside the expected  $T_g$  no melt transition but an undefined low temperature transition at about  $-50^\circ\text{C}$  which was detected only in low temperature DSC or DMA experiments. Two glass transition temperatures can be observed for phase separated block copolymers but had not been expected for these highly irregular, globular structures. In addition, glass transition temperatures measured by DSC were found at  $+34^\circ\text{C}$  (**P1a-O-C12<sub>100</sub>**) and  $+52^\circ\text{C}$  (**P1b-O-C12<sub>99</sub>**), respectively, and therefore are not identical for these two samples even though the degree of modification is very similar. The reason for this might be the differences in the molar mass of the two starting polymers **P1a-OH** ( $\bar{M}_n = 29700 \text{ g/}$

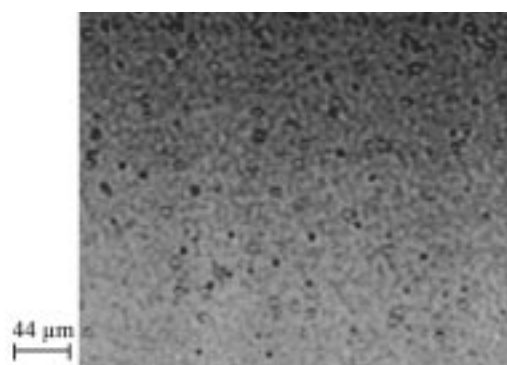


Fig. 5. Light microscopy of **P1b-O-C12<sub>99</sub>** at  $200^\circ\text{C}$  (310 fold magnification)

mol) and **P1b-OH** ( $\bar{M}_n = 58900 \text{ g/mol}$ ) which might have an influence on the observed “phase separation” and the nature of the domains represented by the two thermal transitions. This unusual phase behavior, and the fact that stable, free standing, slightly elastic films could be prepared only from these samples encouraged us to further study the dynamic mechanical and the melt viscosity properties for the completely C12 modified samples.

#### *Phase behavior, dynamic-mechanical properties, and melt rheology*

The appearance of two thermal transitions for **P1a-O-C12<sub>100</sub>** and **P1b-O-C12<sub>99</sub>** leads to the question whether there is a two-phase system. It is possible that those transitions belong to alkyl-rich and aromatic-rich domains, respectively. Light microscopy studies showed a phase separation during the heating of **P1b-O-C12<sub>98</sub>**. A lamellar phase appears at  $90\text{--}93^\circ\text{C}$  and a “droplike” phase at  $108\text{--}110^\circ\text{C}$  (Fig. 5) which is stable up to  $200^\circ\text{C}$ ; however, these “phase transition temperatures” cannot be related to any thermal transition observed by DSC or DMA. One should note that the observed phase separation is on a scale much larger than the size of individual hyperbranched macromolecules. The complex behavior observed in the light microscopy cannot be explained up to now.

Because the unmodified hyperbranched polyester **P1-OH** is a very brittle material due to the absence of entanglements, the formation of a free-standing film failed. By modification of this polymer with alkyl chains the hydrophobic interaction was enhanced which resulted in less brittle and more waxy products. The formation of a free-standing film was achieved by compression molding only of fully modified **P1a-O-C12**. Dynamic mechanical analysis (DMA) on a film of **P1a-O-C12<sub>100</sub>** (Fig. 6) shows a transition at about  $-48^\circ\text{C}$  ( $E''$  maximum). At temperatures higher than  $30^\circ\text{C}$  no results could be obtained since

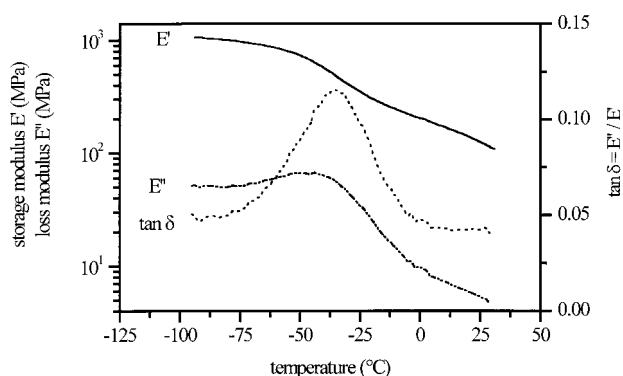


Fig. 6. DMA trace of **P1a-C12<sub>100</sub>** (bending mode, at resonance 3 K/min)

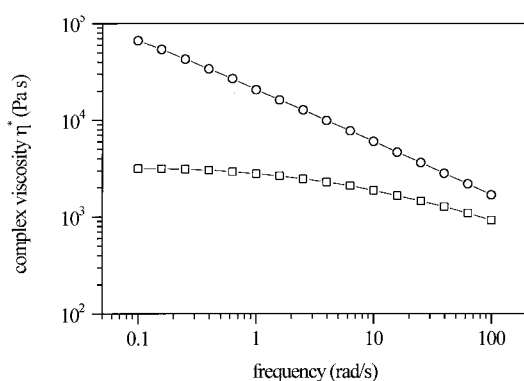


Fig. 7. Complex viscosity of **P1b-OH** at 280 °C (○) and **P1a-C12<sub>100</sub>** at 110 °C (◻) in dependence on the frequency

the resonance frequency limit of this DMA method was reached. The evaluation of the storage ( $E'$ ) and the loss modulus ( $E''$ ) shows that the stiffness of this film is very weak ( $E' < 1000$  MPa). The reason for this is certainly that the ability of the molecules to entangle is reduced compared to linear polymers.

Furthermore, melt rheology was investigated to obtain information on the dynamic-mechanical behavior of the melts. Especially the comparison of the starting polymer **P1b-OH** with the completely modified polymer **P1a-O-C12<sub>100</sub>**, two samples of similar molar mass ( $\bar{M}_n = 58900$  and  $48200$  g/mol, resp.), was of interest. Since the rheology is strongly dependent on the temperature, we compared those sweeps, which were measured 60 K above the corresponding glass transition temperatures: 280 °C for **P1b-OH** and 110 °C for **P1a-O-C12<sub>100</sub>**. In Fig. 7 and 8 the complex viscosity  $\eta^*$ , the storage modulus  $G'$ , and the loss modulus  $G''$  of **P1b-OH** and **P1a-O-C12<sub>100</sub>** are compared.

The measurements indicate that the modification with C12 chains causes a strong decrease in the complex viscosity. The complex viscosity at 1 rad/s is 20000 Pa · s for **P1b-OH** at 280 °C and only 2800 Pa · s for **P1a-O-C12<sub>100</sub>** at 110 °C. While the modified material shows a

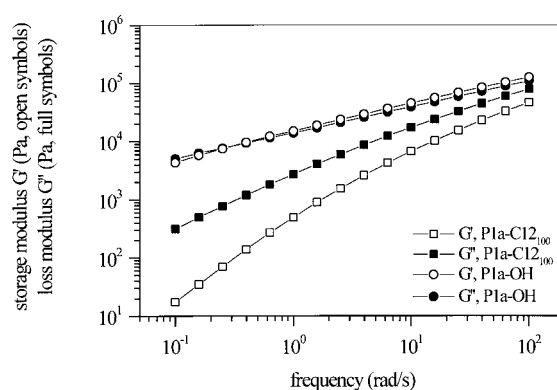


Fig. 8. Storage modulus  $G'$  and loss modulus  $G''$  of **P1b-OH** at 280 °C (○) and **P1a-C12<sub>100</sub>** at 110 °C (◻) in dependence on the frequency

typical behavior for a viscous melt with a plateau at low frequencies, the unmodified material shows a higher dependence of complex viscosity on frequency. The relation between the elastic melt viscosity part ( $G'$ ) and the viscous melt viscosity part ( $G''$ ) of this viscoelastic material is also changed after modification. The **P1b-OH** melt shows elastic and viscous properties in the same quantity. After modification with alkyl chains both moduli are reduced and the viscous behavior becomes dominant.

## Conclusion

A hydroxy-terminated all-aromatic hyperbranched polyester based on 3,5-dihydroxybenzoic acyl was modified with *n*-alkyl acyl chlorides of different chain length. The degree of modification was varied from 11 to 100%. DSC measurements exhibited a complex thermal behavior. The  $T_g$  is reduced with increasing length of the alkyl chain. However, with the appearance of side chain crystallization, the  $T_g$  increases again with further increasing chain length. The reduction of the  $T_g$  can be described as an effect of a reduced endgroup polarity; the crystallization of the side chains results in an intramolecular phase separation and thus the glass transition of the polyester backbone is less influenced by the endgroup modification. The increase of the degree of modification yields a pronounced decrease of the  $T_g$  and for long alkyl chain modification an increase of the side chain crystallization.

The former brittle aromatic hyperbranched polyester could be transformed by C12-alkyl modification to a material, which forms stable, freestanding films. DSC, DMA, and microscopy studies on **P1a-O-C12<sub>100</sub>** and **P1b-O-C12<sub>99</sub>** exhibit a phase separation and the appearance of two thermal transition temperatures but no crystallization. The phase separation which can be observed on the scale of a light microscope has not been understood completely because the branched polymer back-



bone does not allow long range phase separation. It should be understood as formation of alkyl-rich and polyester-rich phases. The melt rheology of the polymers was also investigated. The modification of the aromatic hyperbranched polyester with dodecanoyl acyl chloride yields in a strong reduction of the complex viscosity which opens up applications of this material as a blend component or melt viscosity modifier.

## Experimental part

The monomer 3,5-bis(trimethylsiloxy)benzoyl chloride was prepared as described in ref.<sup>7,8)</sup> Triethylamine, stearoyl chloride, lauroyl chloride, hexanoyl chloride, butyryl chloride and acetyl chloride were obtained from Fluka. Myristoyl chloride and octanoyl chloride were purchased from Merck, palmitoyl chloride was purchased from Aldrich. All chemicals were used as obtained. Details on the synthesis of **P2-OAc** can be found in ref.<sup>11)</sup>

### Polycondensation of 3,5-bis(trimethylsiloxy)benzoyl chloride (**P1b-OH**)<sup>7,8)</sup>

3,5-bis(trimethylsiloxy)benzoyl chloride (20.5 g, 65 mmol) and 1 mol-% ammonium chloride (93 mg) were placed in a flask equipped with a mechanical stirrer, a gas inlet and an outlet. The polycondensation was done in two steps. First the reaction mixture was stirred in a nitrogen stream for 30 min at 170 °C. In a second step vacuum was applied (stirring was not possible any longer) and the reaction proceeded for 5 h without stirring reaching a final vacuum of 0.020 mbar. The crude product was twice dissolved in THF and precipitated into water. After filtration, the product was dried over phosphor pentoxide. Yield: 8.7 g (97%).

IR (KBr): 3420 (m, br, O—H), 3087 (w, C—H), 1743 (s, C=O), 1599 (s, C=C), 1448 (s), 1288 (s, O—H), 1189 (s), 1132 (s, C—OH), 857 cm<sup>-1</sup> (m, C—H).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 10.36 (br, H<sup>linear</sup>, 0.35 H), 9.74 (br, H<sup>terminal</sup>, 0.56 H), 8.06 (m, H<sup>dendritic</sup>, 0.57 H), 7.82 (m, H, 0.31 H), 7.47 (m, H, 0.75 H), 7.00 (m, H, 1.02 H), 6.52 (m, H<sup>terminal</sup>, 0.34 H).

<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 165.1, 164.4, 163.7, 159.6, 159.2, 152.6–152.1, 131.3–130.8, 122.0, 114.9, 108.7.

DB = 62% (from <sup>1</sup>H NMR, compare ref.<sup>8)</sup>).

The polycondensation of **P1a-OH** proceeded similarly.

### General procedure for the modification reaction

All modification reactions were carried out in a nitrogen atmosphere to avoid hydrolysis of the acyl chloride. **P1-OH** (1.36 g, 10 mmol OH groups) was dissolved in 30 ml dry THF; the solution was cooled to 0 °C. Then the acyl chloride (10.5 mmol) and triethylamine (10 mmol) were added. The mixture was stirred for 1 h at 0 °C and for additional 2 h at room temperature. The suspension was filtered and the polymer solution was precipitated twice in water. Isolation of the product was carried out either by filtration or by centrifugation. The product was dried in vacuum over P<sub>2</sub>O<sub>5</sub>.

Characterization for **P1b-O-C12<sub>93</sub>** ( $\bar{M}_n$  = 34000 g/mol; NMR compare Fig. 1 and Scheme 3):

IR (KBr): 3448 (br, m, OH), 3095 (w, C—H), 2923 (s, C—H), 2853 (m, C—H), 1750 (s, C=O), 1596 (m, C=C), 1447 (m, C—H), 1376 (w, C—H), 1130 (s), 813 (w, C—H), 722 cm<sup>-1</sup> (w, C—H).

<sup>1</sup>H NMR (THF-*d*<sub>8</sub>):  $\delta$  = 9.08 (OH<sub>x</sub>), 8.95 (OH<sub>y</sub>), 8.10 (3d), 8.03 (3l), 7.88 (5l), 7.80 (3t), 7.71 (1d), 7.48 (1l, 3x, 5x), 7.43 and 7.38 (3y, 5y), 7.25 (1t), 7.04 (1x), 6.82 (1y), 2.57 (k, CH<sub>2</sub>), 1.70 (j, CH<sub>2</sub>), 1.40 (i, CH<sub>2</sub>), 1.28 (b–h, 7x CH<sub>2</sub>), 0.86 (a, CH<sub>3</sub>)

<sup>13</sup>C NMR (THF-*d*<sub>8</sub>):  $\delta$  = 171.44 (CO—O-alkyl), 163.40 + 163.38 (CO—OPh), 152.51 + 152.39 + 152.31 (O—C<sub>ar</sub>), 132.15 + 131.92 + 131.70 (C<sub>ar</sub>), 122–121 (several signals, CH<sub>ar</sub>), 34.39 to 23.37 (10xCH<sub>2</sub>), 14.30 (CH<sub>3</sub>).

DM = 93% (calculated by <sup>1</sup>H NMR).

### Measurements

The samples were analyzed by NMR using a Bruker ARX 300 (spectrometer operating at 300.13 MHz for <sup>1</sup>H and 75.47 MHz for <sup>13</sup>C) and a Bruker DRX 500 (spectrometer operating at 500.13 MHz for <sup>1</sup>H and 125.77 MHz for <sup>13</sup>C). CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub> and THF-*d*<sub>8</sub> were used as solvent lock and internal standard. FT-IR measurements were performed on a Bruker, IFS 5. A Perkin Elmer DSC 7 (heating rate 20 K/min; temperature range usually –60 °C to +230 °C or to 250 °C; in selected cases measurements were started at –100 °C) was used for the DSC analysis and SEC measurements were carried out using a Waters Liquid Chromatograph with refraction index and UV detector (columns: Waters Ultrastaygel (pore size 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup> Å); solvent THF; polystyrene calibration; the starting polymer was silylated with *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide to avoid adsorption on the columns). For the DMA measurements a DuPont Instruments DMA983 was used and rectangular samples (8.4 mm × 5.1 mm × 1.0 mm) were analyzed in bending mode, at resonance. For these samples a film was prepared from **P1a-O-C12<sub>100</sub>** by compression molding at 120 °C (8 bar); after 45 min the sample was quenched.

Melt rheology was investigated using a ARES rheometer (Rheometrics) with plate-plate-geometry in oscillation mode. Frequency sweeps were performed at 110 °C for **P1a-O-C12<sub>100</sub>** and 280 °C for **P1b-OH** under N<sub>2</sub> atmosphere. The frequency range was between 0.1 to 100 rad/s and a strain of 3% was used which is in the linear viscoelastic range of these materials. **P1a-O-C12<sub>100</sub>** was investigated as film (preparation see DMA), **P1b-OH** as powder.

**Acknowledgement:** The authors would like to thank *DSM Research, Geleen*, for financial support of this work. We are also grateful to *P. E. Froehling* (DSM Research) for his microscopy studies, to *R. Häußler* (IPF) for help with the DMA measurements and to *H. Komber* (IPF) for NMR measurements and help with the signal assignment.

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