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Synthesis and characterization of $A_2 + B_3$-type hyperbranched aromatic polyesters with phenolic end groups

Zhirong Fan, Albena Lederer, Brigitte Voit*

Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, 01069 Dresden, Germany

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ABSTRACT

Hyperbranched (hb) aromatic polyesters with phenolic end groups were synthesized according to the $A_2 + B_3$ approach both, by solution polymerization and by melt (bulk) polymerization with different monomer ratios (A_2:B_3). The hb polyesters produced from solution polymerization exhibited higher yields, molar masses and glass transition temperature (T_g) compared to the products prepared in the melt. The resulting hb aromatic polyesters from the $A_2 + B_3$ approach were also compared with their properties to hb aromatic polymers produced from the well known AB_2 monomer 3,5-bis-(trimethylsiloxy)benzoyl chloride. Both types of hb aromatic polyesters possess high T_g, high thermal stability and good solubility in common organic solvents. A typical melt viscosity behavior with shear thinning effect was also observed for both. Thus similar polymer properties compared to melt-condensed products were obtained with the $A_2 + B_3$ approach by solution polycondensation possessing the advantage of easy monomer availability and much milder polymerization conditions (at room temperature in solution) compared to the AB_2 approach.

1. Introduction

In the last two decades, researchers both from academia and industry showed high interest on hyperbranched (hb) polymers due to their unique chemical and physical properties [1–8]. The easy synthetic accessibility of hb polymers by one-pot synthesis is a great advantage compared to dendrimers and thus, allows their large quantity production in industrial scale.

Among numerous types of hb polymers the family of hb polyesters has been studied in detail. Hb polyesters with the structure ranging from aromatic to aliphatic as well as partial aromatic/aliphatic structures have been investigated in many publications [9–27]. In the reported works, predominantly synthetic strategies based on AB_2 as well as $A_2 + B_3$ approaches were introduced. Hb aromatic polyesters polymerized from AB_2 monomers based on 3,5-dioxybenzoyl building block have attracted special interest [10–19]. However, this highly reactive AB_2 monomer, as well as others, is not easily available in desirable amounts and quality. In that case, the alternative route based on easily available $A_2 + B_3$ monomers can be used for synthesizing hb polyesters as well. Further advantage of the combination of $A_2 + B_3$ monomer in hb polyester synthesis is the better control over possible premature polycondensation due to much higher shelf life of the monomers.

Several hb polyesters based on the $A_2 + B_3$ synthetic strategy have already been reported. Lusic and Fossum presented the $A_2 + B_3$ hb aliphatic polyesters prepared by reaction of fumaric acid and trimethylolpropane, and the ratio of these two reagents was varied [20]. Another hb aliphatic polyester was synthesized by an $A_2 + B_3$ approach using glycerol and adipic acid [21]. Many investigations on the $A_2 + B_3$ route to hb polyesters were also done in the group of Long and several $A_2 + B_3$ hb polyesters were reported by them [22,23]. Furthermore, the theoretical investigations on the kinetics of hb $A_2 + B_3$ system by polycondensation reactions were carried out by Schmaljohann and Voit [24].

Recently, the features of an $A_2 + B_3$ hb aromatic polyester have been reported by Komber et al. [25], focusing on melt polycondensation. In that work the $A_2 + B_3$ hb polyester was synthesized by melt polymerization at 145 °C. Although melt polymerization is widely used in preparation of hb polymers due to the easy one-step technical process, sometimes the solution polymerization is more attractive considering the relatively mild polymerization conditions which reduce the potential of side reactions and facilitate academic studies but can also be interesting for technical production. Actually, in the work of Long [22] the polymerization in solution at room temperature has already been mentioned and led to hb poly(aryl ester)s without gelation. Besides, extensive synthesis and characterization studies for the AB_2 hb

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* Corresponding author. Tel.: +49 (0)351 4658 590; fax: +49 (0)351 4658 565.
E-mail address: voit@ipfdd.de (B. Voit).

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polyester applying solution polymerization instead of melt polycondensation have also been done lately [26,27]. Therefore, in the present work the synthesis of $A_2 + B_3$ hb aromatic polyesters with the reported monomer structures [25] was carried out in a rather easy way: solution polymerization at room temperature. The $A_2 + B_3$ hb polyesters were prepared from two commercially purchased monomers (Scheme 1). As A_2 monomer terephthaloyl chloride (TCl) and as B_3 monomer 1,1,1-tris(4-hydroxyphenyl)-ethane (THPE) were used. For comparison, $A_2 + B_3$ melt polymerization was also carried out using the silylated derivative of THPE: 1,1,1-tris(4-trimethylsiloxyphenyl)ethane (TMS-THPE) as B_3 monomer and TCl as A_2 monomer. In addition, for comparing to the $A_2 + B_3$ synthetic strategy, another hb aromatic polyester with phenolic end groups was prepared by an AB_2 approach based on the well known monomer 3,5-bis(trimethylsiloxy)benzoyl chloride (3,5-BCl) [13,15,17,18]. The thermal properties and melt rheological behavior of these hb aromatic polyesters are of high interest since the motivation for synthesizing them is to explore the possibility of applying them in melt modification of engineering plastics (i.e. linear polyamides) [28].

2. Experimental

2.1. Materials

THPE (≥99%) was purchased from Aldrich; TCl (≥99%), triethylamine (TEA, p.a., with molecular sieve), tetrahydrofuran (THF, p.a., with molecular sieve), and 3,5-dihydroxybenzoic acid (DHBA, ≥99%) were purchased from Fluka; chlorotrimethylsilane (≥99%) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS, ≥98%) were purchased from Merck. The AB_2 monomer: 3,5-bis(trimethylsiloxy)-benzoyl chloride was synthesized according to the previous reports [17,18].

2.2. Characterization methods

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 500 NMR spectrometer (Germany) operating at 500.13 MHz for ^1H and 125.77 MHz for ^{13}C. The solvent DMSO-d_6 [δ (^1H) = 2.50 ppm, δ (^{13}C) = 39.60 ppm] was used as lock and internal standard. The degree of branching (DB) of the hb polyesters can be determined both from ^1H NMR and ^{13}C NMR spectra signals according to the methods introduced in literatures [17,18,25]. The calculation of DB in this work was done as described in Ref. [25] using the modified Frey equation (Eq. (1)) [29]. Here, b_3 indicates fully reacted B_3 monomer (dendritic unit) and Bb_2 represents a linear unit.

$$DB_{Frey} = \frac{2\cdot[b_3]}{2\cdot[b_3] + [Bb_2]} \qquad (1)$$

Size exclusion chromatography (SEC) measurements in distilled THF (Acros Organics, p.a.) containing 0.025% BHT were performed with a PLgel mixed B column (Polymer Laboratories, UK). The system consists of a pump from WGE Dr. Bures (Germany), a multi-angle laser light scattering (MALLS) detector (DAWN EOS, $\lambda = 690$ nm, Wyatt Technologies, USA) and a refractive index (RI) detector (Knauer, Germany). The flow rate was 1.0 mL/min at a temperature of 25 °C.

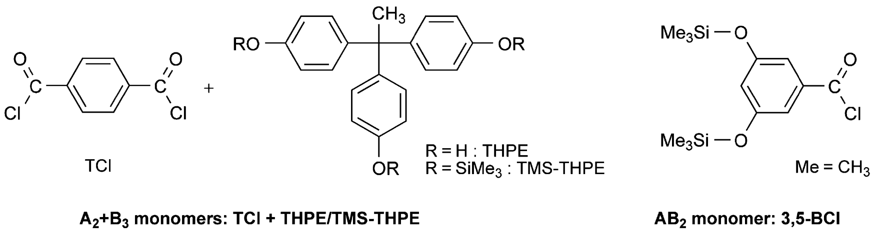
Due to the strong interactions between the AB_2 hb polyester and the SEC column, asymmetric flow field-flow fractionation (A4F) was used to determine the molecular weight of the AB_2 hb polyester. A4F was performed on Eclipse 3 (Wyatt Technologies Europe, Germany) with a long channel, PEEK cover plate and an isocratic pump and degasser of 1200 series (Agilent Technologies, USA) [27]. Detection was carried out by a Mini-DAWN light scattering detector ($\lambda = 690$ nm, Wyatt Technologies, USA) and a RI detector (Knauer, Germany). Distilled THF (Acros Organics, p.a.) containing 0.025% BHT was used as solvent for the sample preparation as well as eluent for the experiments. The refractive index increment, dn/dc of 0.25 mL/g for all light scattering calculations was determined using a differential refractive index detector of WGE Dr. Bures (Germany) at a wavelength of 620 nm and a temperature of 25 °C.

The pyrolysis gas chromatography–mass spectrometry (GC–MS) measurements were done using a gas chromatograph 5890 (Hewlett Packard, USA) with mass-selective detector 5971A, and pyrolysator Pyroprobe 2000 (CDS Instruments, USA) at the required temperatures. The samples were filled into glass tubes and preheated in an interface at 140 °C.

Differential scanning calorimetry (DSC) was done using a DSC Q1000 Advanced T_{ZERO}™ (TA Instruments, USA) for the determination of T_g. The DSC measurements were performed under N_2 in the range between −80 and 340 °C at a heating rate of 10 K/min as cycles consisting of 1st heating–cooling–2nd heating scans. The T_g of the hb polymers was determined from the 2nd heating run by half step method.

Thermal gravimetric analysis (TGA) was done on TGA7 (Perkin Elmer, USA) and TGA-Q5000$_{IR}$ (TA Instruments, USA) under a nitrogen (N_2) atmosphere. Both, dynamic and isothermal TGA measurements were performed. Dynamic TGA was carried out at a temperature range of 40–700 °C using a heating rate of 10 K/min. The isothermal TGA was performed at 320 °C. After preheating at 40 °C for 10 min the samples were heated up to 320 °C within 5 min and then the samples were investigated isothermally for about 1 h.

Melt rheological measurements were performed using a Rheometrics Scientific ARES (Germany) with plate–plate-geometry in oscillation mode in a N_2 environment at 320 °C. The plate diameter was 25 mm and the gap ranged from 0.8 to 1.2 mm. A frequency range between 0.1 and 100 rad/s and a strain within the linear viscoelastic range were used. The samples were investigated as small pieces of strain after thermal processing. Dynamic frequency sweep (strain control) mode test was used to determine the melt viscosity and storage/loss modulus. With the same instrument a dynamic time sweep test (at constant temperature 320 °C and frequency of 1 rad/s) was used for indicating the structural changes (crosslinking or decomposition) of the hb polymers during the measurements.



Scheme 1. Monomers for synthesis of the hyperbranched aromatic polyesters.

2.3. Synthesis of $A_2 + B_3$ hb polyester by solution polymerization

The $A_2 + B_3$ hb polyester was synthesized by solution polymerization of monomers A_2 (TCl) and B_3 (THPE) using different monomer ratios (A_2:B_3). The used monomer amounts of TCl were 1.33 g (6.55 mmol) and of THPE were 1.34 g (4.38 mmol), 2.0 g (6.53 mmol), 2.68 g (8.75 mmol) and 4.01 g (13.1 mmol), corresponding to the A_2:B_3 molar ratios of 3:2, 1:1, 3:4 and 1:2 respectively. The monomers were dissolved separately in THF to give two monomer solutions with the concentration of 46 mmol/L. In another series of experiments the concentration of the monomer solutions was increased to 57 mmol/L. About 1.8 mL of TEA (13 mmol), used as trap for HCl formed during polycondensation, were added to the THPE solution. In a dry three-necked flask equipped with gas inlet, outlet, condenser and magnetic stirring bar, the TCl solution was dropped into the THPE solution within ca. 1.3 h under N_2 stream at room temperature. The reaction mixture was stirred over 24 h to ensure high conversion and then filtrated out. The filtrated reaction solution was dropped into about 8- to 10-fold excess volume of methanol for precipitation. During precipitation the remaining acid chloride groups were converted to methyl esters simultaneously. After filtration the final product was collected and dried in a vacuum oven at 50 °C with drying agent for several days to give the $A_2 + B_3$ hb polyester as white brittle solid.

^{1}H NMR (500 MHz, DMSO-d_6, ppm): $\delta = 9.35$ (s, OH_{linear}), 9.26 (s, $OH_{terminal}$), 8.32 (s, ArH), 7.05–7.4 (m, ArH), 6.55–6.97 (m, ArH), 3.91 [s, C(O)OCH_3], 2.25 (s, $CH_{3,dendritic}$), 2.15 (s, $CH_{3,linear}$), 2.05 (s, $CH_{3,terminal}$). ^{13}C NMR (125 MHz, DMSO-d_6, ppm): $\delta = 166.65$, 165.50, 163.95, 155.63, 155.37, 148.33, 148.56, 148.78, 147.90, 147.10, 146.39, 139.35, 138.58, 135.43, 133. 53, 132.59, 130.29, 130.02, 129.78, 129.52, 129.21, 121.43, 121.18, 120.92, 114.85, 114.63, 114.41, 51.53, 51.02, 50.50, 30.43.

2.4. Sampling during solution polymerization

During the solution polymerization (including the slow addition of TCl solution to the THPE solution), several samples were taken out of the reaction system after certain reaction times and the polymerization reaction was stopped by drop-wise pouring the samples in methanol. At every time about 20 mL reaction solution were taken out of the reaction flask by syringe, filtrated by filter, and the filtrate was dropped into ca. 200 mL methanol for precipitation. The solvent (THF and methanol) was removed completely at room temperature by evaporation under reduced pressure (water pump). The obtained solid was then collected and dried in vacuum oven with drying agent before further characterizations.

2.5. Synthesis of $A_2 + B_3$ hb polyester by melt polymerization

In melt polymerization TMS-THPE was used as B_3 monomer. It was synthesized from HMDS, chlorotrimethylsilane and THPE. The synthesis of TMS-THPE and the melt polymerization of TCl and TMS-THPE were carried out according to the reported procedure [25]. The monomer ratios of TCl to TMS-THPE were also varied in the same values as those in solution polymerization. After polymerization (about 4.5–5 h), the raw product was dissolved in dry THF (with molecular sieves), then the THF solution was drop-wise added in ten times volume of methanol to form the hb polyester with hydroxyl end groups. After filtration the hb polymer was collected and dried in vacuo at 50 °C with drying agent for several days to give the product as white powder. These products showed the same NMR spectra as those of the polymers prepared from solution polymerization.

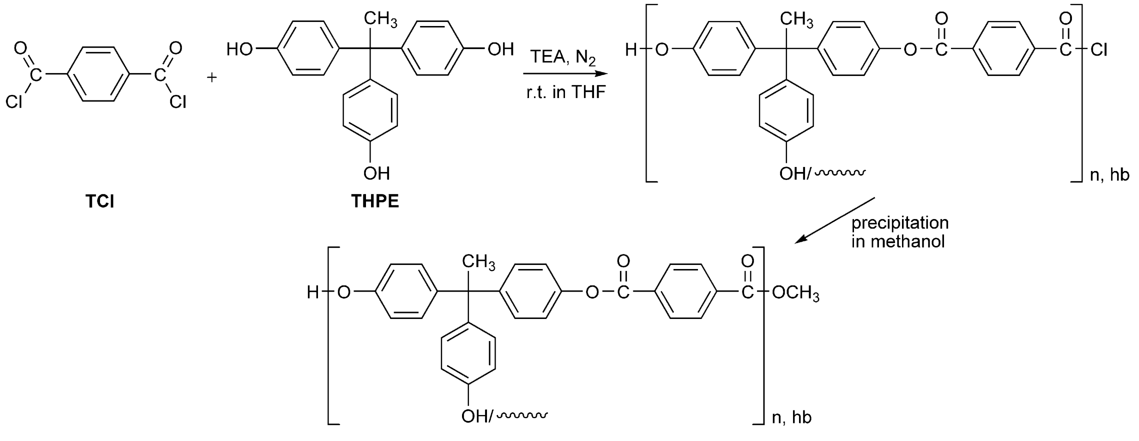
2.6. Thermal processing of hb polyesters

Prior to melt rheology studies, both the AB_2 hb polyester and the $A_2 + B_3$ (3:4) hb polyester from solution polymerization were thermally processed by a twin-screw mini-compounder (Micro-5 Compounder, DSM Xplore) with a batch volume of ca. 5 mL. Both the barrel and the sample temperatures were controlled. Air was used for cooling. The hb polyesters were used as powder for processing. The thermal processing of them was performed at 320 °C for ca. 5 min. The hb polyesters were dried in vacuum oven at 50 °C together with drying agent for one week prior to this thermal processing. The screw speed for processing was 100 rpm. The total amount of the hb polymer for processing was about 2.5 g.

3. Results and discussion

3.1. Synthesis of $A_2 + B_3$ hb polyesters

The $A_2 + B_3$ hb polyesters were synthesized by both solution and melt polymerization in this work. For the polymerization of $A_2 + B_3$ monomers in solution, cross-linked products were obtained when the diluted solution of B_3 was added to the diluted A_2 solution due to a high local concentration of the acid chloride functionality (A) [22]. In order to avoid the formation of insoluble products, in the present work, the polycondensation of TCl (A_2) and THPE (B_3) was performed in dilute solution with adding slowly the TCl solution to the THPE solution (Scheme 2). All of the polymerizations were conducted at room temperature (r.t.) due to the high reactivity of the acid chloride (TCl). The molar monomer ratio and the monomer



Scheme 2. Schematic route of the solution polymerization of TCl and THPE.

concentration were varied. Finally, the products were precipitated in methanol which stopped the polycondensation and could result in $A_2 + B_3$ hb polyesters with phenolic and methyl ester end groups theoretically.

The synthesis was carried out using different monomer ratios (A_2:B_3 = 3:2, 1:1, 3:4 and 1:2). These four monomer ratios correspond to a systematic variation of the functionality ratio A to B: the 3:2 molar monomer ratio results in a stoichiometric amount of the functional groups A and B; the 1:1 molar monomer ratio results in excess of B functionalities (A:B = 2:3); the 3:4 molar monomer ratio possesses an A:B = 1:2 ratio of the functional groups as a direct comparison to the hb AB_2 system; and the 1:2 molar monomer ratio has an even higher excess of B functionalities (A:B = 1:3). To avoid any confusion, in the following content only the values of molar monomer ratios (A_2:B_3) will be mentioned.

For comparison $A_2 + B_3$ hb polyesters were also synthesized by melt polymerization of TCl (as A_2 monomer) and TMS-THPE (as B_3 monomer) at 145 °C using different monomer ratios, A_2:B_3 = 3:2, 1:1, 3:4 and 1:2, according to previous publication [25]. The resulting $A_2 + B_3$ hb polyesters obtained both from solution and melt polymerization were characterized and the influence of the variation of the monomer ratios (A_2:B_3) on the properties of resulting hb polymers was discussed.

3.2. Characterization of $A_2 + B_3$ hb polyesters synthesized by solution polymerization

General characterization results of the obtained products are summarized in Table 1. Obviously, the monomer ratio has a crucial influence on the properties of the resulting $A_2 + B_3$ hb polyesters. With the functionality ratio shifting toward the stoichiometric situation polymers with higher yields and higher molecular weights were obtained, but higher possibility for gelation was observed as well. A typical negative aspect of an $A_2 + B_3$ system is the gelation which can be avoided only by termination of the reaction before the gel point when approaching the stoichiometric functionality ratio. In the described system at the monomer ratio A_2:B_3 = 3:2 gelation occurred during polymerization under all studied conditions. Depending on the monomer concentration in the reaction solution, gelation could be observed also at the monomer ratio of 1:1 (P4): under identical conditions, a more concentrated solution led to faster polymer build-up and thus, to earlier gelation. As described already by Flory [30] and Odian [31], the theoretical gel points for the 3:2 and 1:1 ratios of A_2:B_3 can be calculated to 70.7% and 86.6% conversion of A functionalities, respectively. And thus gelation can not be avoided for the 3:2 products when the critical functionality conversion is reached which is very likely due to the high reactivity. Also the hb polyester P3 has been isolated very close to the gel point as the very broad polydispersity (M_w/M_n) indicates.

As expected the yield and molar mass decreased with decreasing the content of A_2 monomer (TCl) meaning higher excess of B_3 monomer. Off-stoichiometric conditions shift the critical conversion to higher values and it can even be fully avoided but then, only low molar mass products can be achieved. The decreasing yield can be explained in this case with the fractionation of the low molecular weight oligomers during the precipitation and filtration procedures. This was verified by SEC investigations of the raw products without fractionation. In the oligomeric region DB as calculated by the Frey equation as outlined in Ref. [25] is still dependent on the degree of polymerization, and thus lower values than those of higher molar mass products result. Clearly, lower molar mass products exhibit also lower glass transition temperatures.

Although the best yields and the highest molar masses were obtained by the solution polymerization with the monomer ratio of 1:1, better control over the synthetic experiment and the properties of resulting material, i.e. gelation, acceptable yield, T_g values as well as reasonable molar mass, were achieved by polymerization with monomer ratio of 3:4.

Table 1
Characterization of the $A_2 + B_3$ hb polyesters from solution polymerization.

$A_2 + B_3$ hb polyesters	A_2:B_3	Yield (%)	DB_{Frey}[a] (%)	T_g (°C)	M_w[b] (g/mol)	M_w/M_n	Temperature of 10% weight loss[c] (°C)	Monomer conc.[d] (mmol/L)
P1[e]	3:2	–	–	>300	–	–	–	46
P2[e]	3:2	–	–	–	–	–	–	57
P3	1:1	85	52	268	28,500	9.5	427	46
P4[e]	1:1	84	–	>300	–	–	–	57
P5	3:4	70	46	223	11,000	2.3	398	46
P6	3:4	71	46	219	10,000	2.5	413	57
P7	1:2	46	40	204	4400	1.4	408	46
P8	1:2	51	40	199	4500	1.5	357	57

[a] Determined from ^{13}C NMR signal intensities of dendritic unit (51.53 ppm), linear unit (51.02 ppm) and terminal unit (51.5 ppm), relative error: 10%; calculation was done according to Ref. [25].
[b] Results derived from SEC measurements with LS detector.
[c] Values determined by dynamic TGA measurements under nitrogen.
[d] Monomer concentration in reaction solutions.
[e] Insoluble in solvent due to gelation.

3.2.1. NMR investigation of $A_2 + B_3$ hb polyesters from solution polymerization

Information about structures of the $A_2 + B_3$ hb polyesters as well as DB was provided by NMR measurements. Unlike the well investigated classical hb polymers produced from AB_n monomers, defining the structure of $A_2 + B_3$ hb polymer system precisely is still difficult to fulfill. Herein the numbering of atoms and the assignments of the NMR signals from different units (terminal, linear and terminal subunits) of the $A_2 + B_3$ hb polyesters prepared by solution polymerization was done according to the reported method [25].

Fig. 1 shows the ^{13}C NMR spectra of the $A_2 + B_3$ hb aromatic polyester synthesized by solution polymerization with a monomer ratio of 3:4. Polymerizations with other monomer ratios resulted in almost the same NMR spectra except the peak shapes, higher A_2 monomer ratios led to spectra with somewhat broader signals due to the higher molar mass products achieved. Since the hb polymer was obtained from the precipitation in methanol and both monomers (TCl and THPE) were soluble in methanol or was able to react with methanol, the uncondensed monomers (TCl or its derivative and THPE) should be removed theoretically by the precipitation.

As expected, the good identification of different atoms and the well-separated signals corresponding to the different subunits from terminal (***t***), linear (***l***) and dendritic (***d***) parts verified the hyperbranched structures of the $A_2 + B_3$ hb polyester. Therefore, the ratios of those subunits in the hb polymer can be estimated easily according to the intensity of the corresponding signals. As a result, the DB (see Experimental part) and the conversion of the monomers can be determined. A signal of a trace of carboxylic acid group was detectable, which was most probably from the hydrolyzed TCl during experiment.

3.2.2. Molar mass determination of $A_2 + B_3$ hb polyesters from solution polymerization

Both refractive index (RI) and multi-angle laser light scattering (MALLS) detector were used in SEC measurements to determine the molecular weight of the $A_2 + B_3$ hb polyesters synthesized from different monomer ratios and with different monomer concentrations (Fig. 2). Gelation was observed for the polymerizations carried

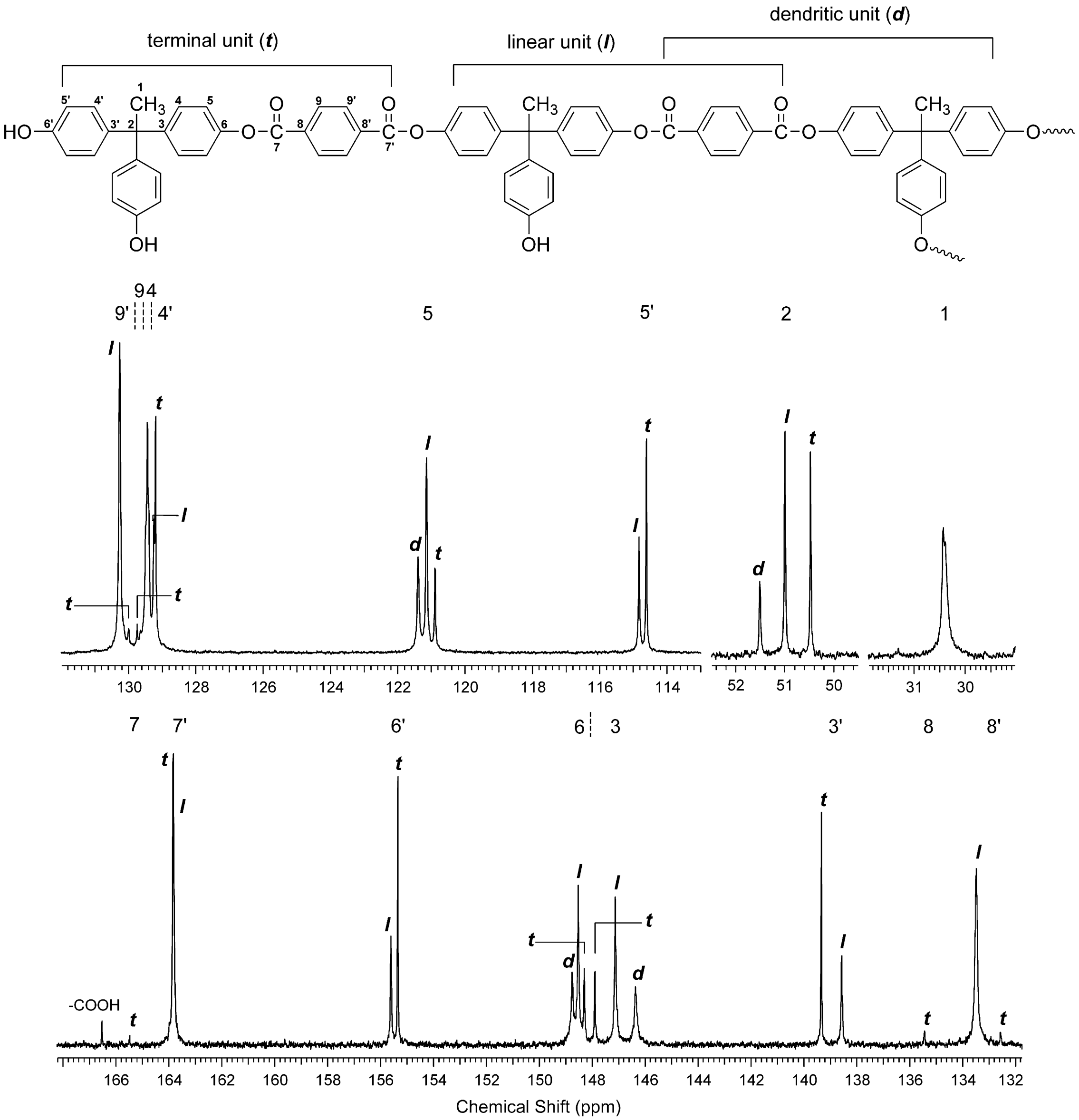


Fig. 1. ^{13}C NMR spectra (in DMSO-d_6) of the $A_2 + B_3$ (3:4) hb polyester obtained from solution polymerization and the different structural units for signal assignments.

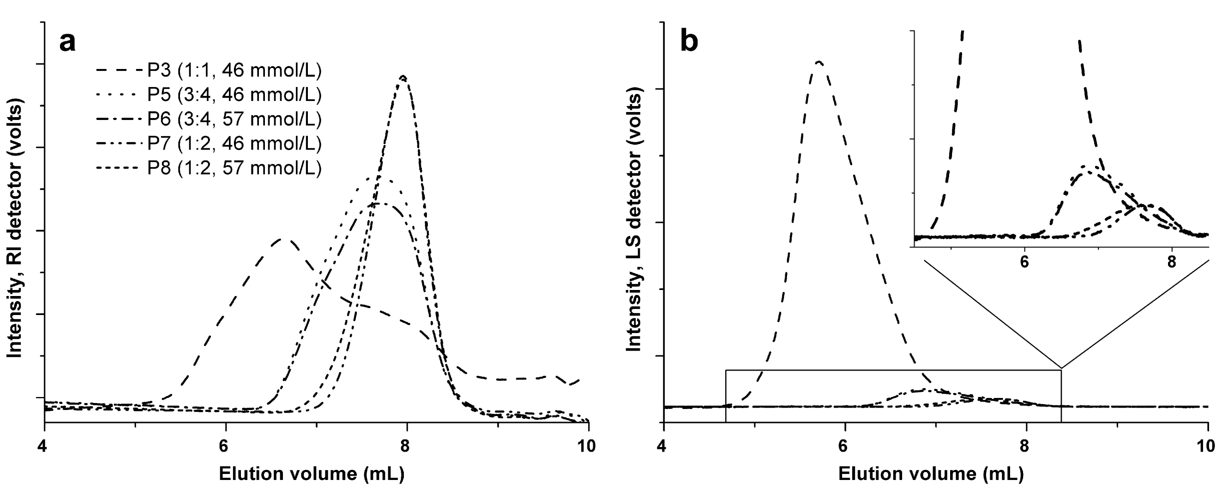


Fig. 2. SEC measurements with (a) RI detector, (b) LS detector of the $A_2 + B_3$ hb polyesters prepared from solution polymerization with different molar monomer ratios and monomer concentrations.

out with higher A_2 ratio (3:2 and 1:1 at monomer concentration of 57 mmol/L), which resulted in insoluble polymers and hence SEC measurements of them were not possible. It is clearly visible that with the functionality ratio approaching stoichiometry, the SEC curves show a broadening of the peaks due to increasing polydispersity of the samples as theoretically predicted [32]. The SEC curve of P3 (Fig. 2a) exhibited a peak with shoulder in the high molar mass region, which points to the beginning of crosslinking. A multimodal distribution is not visible in the LS curve of P3 (Fig. 2b) due to the fact that LS detector indicates preferably higher molar masses and the lower molar masses in a broadly distributed sample are underestimated or completely ignored. The shapes of the chromatograms of the samples with A_2:$B_3 < 1$ show distributions independent on the monomer concentration, supporting our suggestion that the different monomer concentration of reaction solution results in almost identical polymer structures, while at higher A_2 monomer ratios the high molar mass species are stronger represented.

3.2.3. *Investigation on the samples taken out during the $A_2 + B_3$ solution polymerization*

Efforts were also done to clarify the kinetics of the solution polymerization of the $A_2 + B_3$ monomers. For this purpose several additional experiments were carried out. During the experiments, samples were frequently taken out from the reaction system and poured immediately in methanol for stopping the condensation reaction. After that the resulting experimental samples were collected for characterizations to provide further information about the structural development and the molar mass build-up of the hb polymer as well as the conversion of the monomers during the polymerization.

According to the analytical results, plots of the structural development of the samples prepared by solution polymerization with monomer ratio of 1:1 depending on the reaction time are shown in Fig. 3a. The data were calculated based on the signal intensities of the different subunits, dendritic (***d***), linear (***l***) and terminal (***t***) units, in the NMR spectra and normalized by dividing through the original B_3 amount. It is observed that after a reaction time of ca. 1.3 h no more changes for intensities of the signals from the subunits were detectable by NMR. The time counting started as the first drop of the TCl (A_2) solution was added to the reaction solution. Among all of the data points, the third one (ca. 1.3 h) was from the sample taken out when the addition of TCl solution was finished. Within this reaction time the hyperbranched structure (***d***, ***l***, ***t*** units) was developing with consumption of the monomer B_3. However, after that all the values kept almost constant and no further conversion of B functionality was visible, which indicated that the polymerization was already accomplished. Since the slow addition of the highly reactive monomer was used a relatively fast reaction could have been expected.

The molar mass build-up and the DB development during the solution polycondensation are shown in Fig. 3b. The results indicate clearly that in the very beginning, typical for a polycondensation, only oligomers were formed since no high molar mass products were detected. However, at the third data point (ca. 1.3 h), the product with very high molar mass was detected, followed by an additional fast decrease in molar mass of the polymers. This unusual molar mass development behavior was also observed in another experiment with a monomer ratio of 3:4, which leads to the assumption that a kind of molar mass equilibrium takes place in the $A_2 + B_3$ solution polymerization process. It has to be noted that for the second sample, besides a polymer peak at $M_w = \sim 15{,}000$ g/mol, a small peak in the oligomer region was also detected by SEC. In addition, the polydispersity of the samples increased significantly from 1.2 (the second point) to 4.3 (the third point) and even higher than 6 for the following points. These facts indicate that due to so far unknown reasons a fast molar mass build-up takes place in the beginning of the reaction followed by a slower process leading to lower molar mass products as monomer conversion proceeds. This results finally in very broadly distributed products with multimodal SEC traces and determined molar mass values below those of the isolated product after 1.3 h. After about 2.3 h (the fourth point, Fig. 3b) practically no further change for all the values could be observed, which is an indication for a nearly complete reaction with 93% B_3 conversion and products with 60% degree of branching and 32 kg/mol weight average molar mass. Thus, for future studies it is clear that originally chosen reaction time of 24 h can be significantly shortened in the solution polymerization process.

3.3. *Comparison with $A_2 + B_3$ hb polyesters synthesized by melt polymerization*

Similar to the results of the $A_2 + B_3$ hb polyesters prepared by solution polymerization, an obvious dependence of molar mass on monomer ratios (A_2:B_3) was observed for the polymers produced by melt polymerization (Table 2). The polydispersity values (M_w/M_n) from SEC measurements showed that melt polycondensation with monomer ratios of 1:1 and 3:2 resulted in the hb polymers with very broad molar mass distribution but gelation did not yet

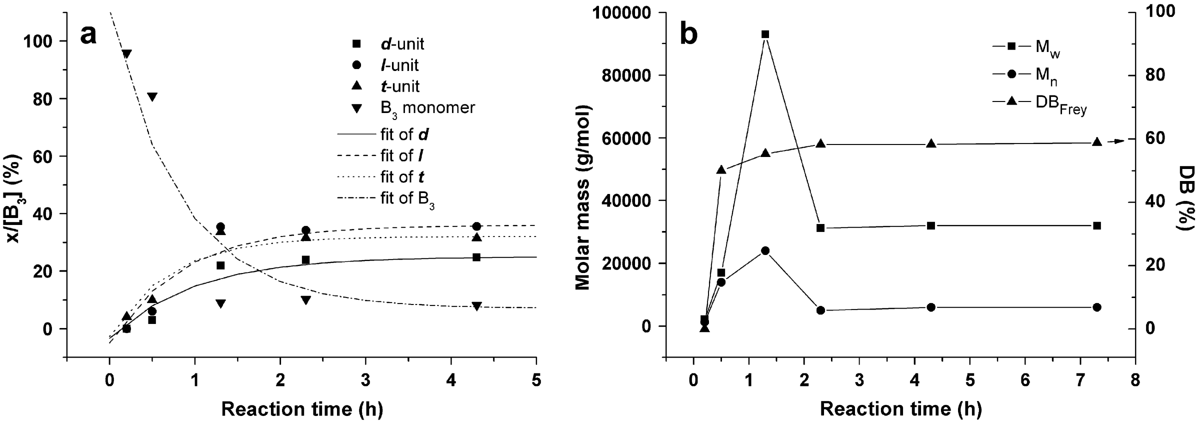


Fig. 3. Investigations on the samples taken out during the solution polymerization of $A_2 + B_3$ monomers (1:1) with a monomer concentration of 46 mmol/L: (a) development of the subunits (***d***, ***l***, ***t***) and the B_3 monomer contents, (b) molar mass and DB results in dependence on the reaction time.

Table 2
Characterizations of the $A_2 + B_3$ hb polyesters prepared from melt polymerization.

$A_2 + B_3$ hb polyester	A_2:B_3	Yield (%)	DB_{Frey}[a] (%)	T_g (°C)	M_w[b] (g/mol)	M_w/M_n	Temperature of 10% weight loss[c] (°C)
P9	3:2	41	–	194	68,000	35.0	429
P10	1:1	51	47	210	33,000	20.7	439
P11	3:4	47	41	200	4300	1.5	407
P12	1:2	–	35	200	3800	1.4	402

[a] Determined from ^{13}C NMR signal intensities of dendritic unit (51.53 ppm), linear unit (51.02 ppm) and terminal unit (51.5 ppm), relative error: 10%; calculation was done according to Ref. [25].

[b] Results derived from SEC measurements with LS detector.

[c] Values determined by dynamic TGA measurements under nitrogen.

occur. A tendency of an increasing molar mass distribution with the monomer ratio getting close to the stoichiometric situation was also observed.

In general, the $A_2 + B_3$ hb polyesters synthesized by solution polymerization exhibited higher yields and higher molar masses but also a higher tendency for gelation than those of the hb polymers produced from melt polymerization using the same monomer ratios. As mentioned in the previous publication [25], the volatilization of A_2 monomer (TCl) can result in a change of the composition of the reaction mixture during the melt polymerization. This can lead to off-stoichiometric conditions for avoiding gelation in P9 and an even higher excess of B_3 for the other samples limiting the development of the polymer structure and resulting in lower yields and molar masses compared to those of the hb polymers prepared in solution.

3.4. Comparison between the $A_2 + B_3$ and AB_2 hb polyesters

In order to compare the hb polymers prepared by different synthetic strategies, besides the $A_2 + B_3$ approach, polycondensation of the well known AB_2 monomer 3,5-bis-(trimethylsiloxy)benzoyl chloride was also carried out according to the previously reported method [17,18]. Fully soluble aromatic AB_2 hb polyesters with high glass transition temperatures ($T_g \sim 220$ °C) were obtained (Table 3). Polymers with a DB of about 55% in very high yield (98%) were achieved in both cases. Different from the solution polymerization, a longer polymerization time resulted in an AB_2 hb polyester (P14) with higher molar mass, which corresponds also to the results reported in previous works [12,13,15]. This difference was related to the different driving force for the molar mass build-up in solution and melt polymerizations [22]. Comparison between the results of the $A_2 + B_3$ and AB_2 hb polyesters synthesized in the melt leads to the conclusion that AB_2 monomer results in higher molar mass products with a higher DB without any danger of gelation during polymerization.

3.5. Thermal properties

Detailed information about the thermal stability of the hb polyesters was provided by DSC and TGA investigations. Products without gel content and molar masses above 10,000 g/mol show a comparable T_g of 210–220 °C no matter what synthetic route was chosen. Dynamic TGA results show that the maximum rate of decomposition of all $A_2 + B_3$ hb polyesters prepared from different monomer ratios (Table 1, Fig. 4) occurs at 505 °C with the 10% weight loss at about 400–420 °C, which points to a relatively high thermal stability.

Table 3
Characterization of the AB_2 hb polyesters.

AB_2 hb polyester	Reaction time (h)	Yield (%)	DB_{Frey}[a] (%)	T_g (°C)	M_w[b] (g/mol)	M_w/M_n	Temperature of 10% weight loss[c] (°C)
P13	5	98	56	220	45,000	2.0	373
P14	7	98	55	221	147,000	3.4	380

[a] Determined from ^1H NMR signal intensities of dendritic unit (7.7–8.18 ppm), linear unit (7.38–7.58 ppm) and terminal unit (6.53 ppm), relative error: 10%; calculation was done according to the method of Frey [29].

[b] Determined by A4F measurements with RI and LS detector.

[c] Values determined by dynamic TGA measurements under nitrogen.

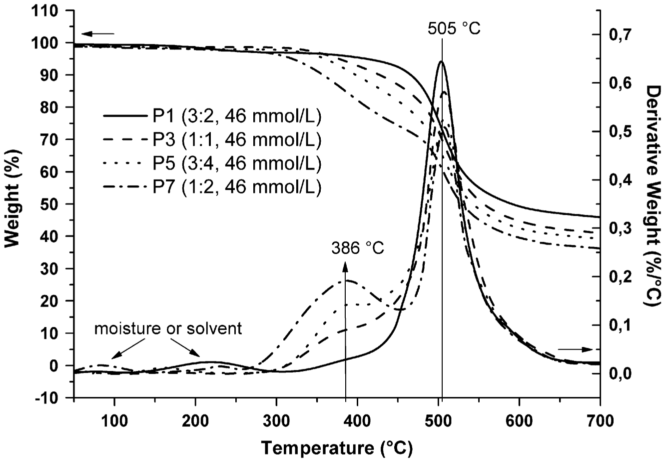
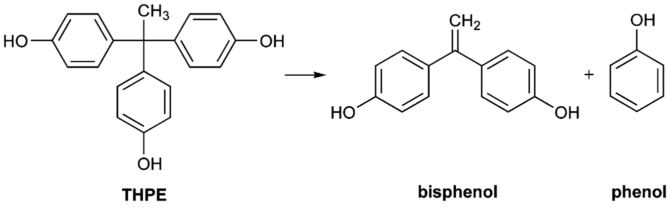


Fig. 4. Dynamic TGA measurements of the $A_2 + B_3$ hb polyesters prepared from solution polymerization with different molar monomer ratios.

The mass losses at 50–280 °C are caused by the evaporation of remaining solvent or absorbed moisture in the samples according to GC–MS analysis. However, with the monomer ratio changing from 3:2 to 1:2 a more and more pronounced earlier degradation step (shoulder) at approx. 386 °C can be observed. The origin of this shoulder was then followed by pyrolysis GC–MS investigations on these samples.

The results of the pyrolysis GC–MS studies at 225, 380 and 505 °C gave a clear indication of phenol development, and the excess of B_3 in the starting monomer ratio increased the amount of released phenol. Formation of phenol was found in the reported work [25] as well, however as a product of a side reaction during the melt polymerization at 185 °C and it was assigned to the reaction shown in Scheme 3. In that reported work the evolved bisphenol from decomposition of the monomer THPE was found to participate in the melt polymerization.

In our case, only small and comparable amounts of B_3 monomer (THPE) were detected by NMR in all precipitated $A_2 + B_3$ hb polymers. However, the TGA curves of the same samples clearly showed dependence of the peak intensity for the phenol evolution on the used molar ratios of two monomers. Therefore, the formation of the observed phenol evolution is not ascribed to a side reaction of B_3 monomer as in Ref. [25] but to the decomposition of structural units containing free phenolic end groups, especially the terminal units. Decomposition of linear units (***l***) is less probable than that of the terminal units since it requires a rearrangement of the main chain.



Scheme 3. Side reaction of THPE in melt polymerization at 185 °C [25].

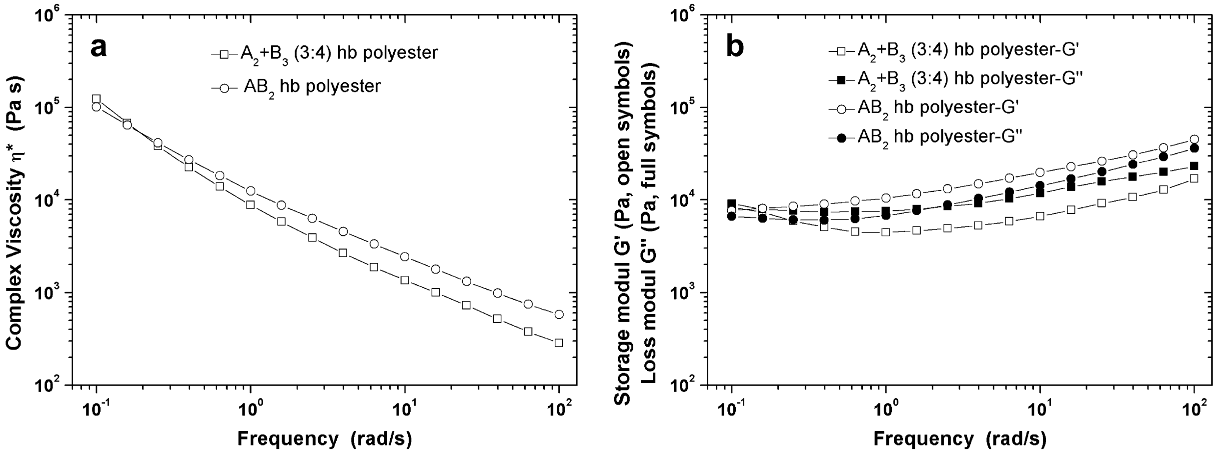


Fig. 5. Melt rheological behaviors of the hb polyesters after thermal processing at 320 °C: (a) complex viscosity vs. frequency; (b) storage modulus G' and loss modulus G'' vs. frequency, investigated at 320 °C.

With increasing molar ratio of B_3 monomer relatively lower molar mass products were obtained, which should also lead to an increase of the molar ratio of the terminal units (***t***) in the polymer and this was verified by the NMR analysis. Comparison of the SEC results in Table 1 with the above TGA results (Fig. 4) shows that the hb polyester P7 with the highest amount of low molar mass species and also the relatively highest amount of terminal units (prepared from the highest excess of B_3 monomer) exhibited the most pronounced earlier degradation step as well in the TGA curves. This supports the assumption that the degradation starts mainly at the terminal B units.

Both, the AB_2 hb polyester (P14) and the $A_2 + B_3$ (3:4) hb polyesters from solution polymerization (P5) were further investigated by the isothermal TGA measurements at 320 °C. This temperature was applied because it is required for both hb polyesters when they are melt mixed with linear polymers as modifiers [28]. The isothermal TGA results showed that after a slight weight loss due to water or solvent evaporation at the beginning of the measurement, a small plateau was reached, after that the main degradation of the hb polymers started. Although P14 showed a comparable T_g as that of P5, the iso-TGA results indicated clearly that in the whole measurement's range P5 exhibited a quite lower mass loss than that of P14 at 320 °C. This difference most probably could be ascribed to the different content of phenolic end groups in them. The amounts of phenolic end groups per gram of polymer were calculated from the ^{1}H NMR spectra. The results show that there are about 7.5 mmol of phenolic end groups in one gram of P14, which is 2.9 times of that in P5 (2.6 mmol/g). Higher amount of phenolic end groups also increases the amount of moisture in the polymer absorbed from ambient environment, that's why P14 exhibited a much higher mass loss (2.5%) at the beginning of the iso-TGA curve than that of P5 (ca. 1%). Furthermore, post-polymerization reaction may occur in P5, which can lead to a molecular weight increase and consequently a better thermal stability. Similar results were also found by Turner et al. [15] early on and were verified later on comparing the polymers prepared from both solution and melt polymerization [26,27].

3.6. Melt rheological behavior

The prime motivation for synthesizing these two types of hb aromatic polyesters was to use them in the modification of linear polyamides by melt mixing [28]. Therefore, the melt rheological behavior of both, the AB_2 hb polyester and the $A_2 + B_3$ (3:4) hb polyester from solution polymerization was also of high interest. Both hb polyesters were thermally processed at 320 °C and investigated by melt rheological measurements. Thermal processing by a mini-compounder needs at least 2-3 g of the materials, therefore the hb polyesters from different synthetic batches but with comparable analytical data as those described above were used and compared to each other in this section.

The complex (melt) viscosity of the AB_2 hb polyesters decreased with increasing frequency in a nearly linear relationship (Fig. 5a) which is characteristic for the rheological behavior of hb polymers with phenolic or carboxylic end groups [18,33,34]. In contrast to the AB_2 hb polyester, the complex viscosity of the $A_2 + B_3$ (3:4) hb polyester deviated slightly from the linear relationship with frequency (≤1 rad/s). As mentioned above, in the case of $A_2 + B_3$ hb polyesters the polycondensation had to be stopped before occurring of gelation. Consequently, the resulting $A_2 + B_3$ hb polyester could still contain active groups, which could react with each other to develop a post-polymerization molar mass build-up during the thermal processing. Therefore the positive deviation of complex viscosity in the low frequency range which is sensitive to the molecular structure, could be the effect of further intermolecular reactions at the high temperature processing. The plots of storage (G') and loss modulus (G'') against frequency (Fig. 5b) show a relaxation behavior in the range of 0.1–1 rad/s which is typical for the branched polymers. The results indicate that the $A_2 + B_3$ (3:4) hb polyester exhibits a predominately viscous behavior ($G'' > G'$), however the AB_2 hb polyester acts as elastic material ($G'' < G'$).

In addition, the thermally unprocessed hb polyesters were also studied by the rheological measurements using the time sweep mode test (at constant temperature of 320 °C and frequency of 1 rad/s) in order to check the structural changes (crosslinking or decomposition) of the hb polyesters during high temperature processing. A continuous increase of melt viscosity (from 6×10^4 to 9×10^4 Pa s within 5 min) of the $A_2 + B_3$ (3:4) hb polyester obtained from solution polymerization was observed. However, the melt viscosity of the AB_2 hb polyester kept almost constant in the same measurement. The results of the $A_2 + B_3$ system are again typical for the occurrence of a post-polymerization reaction leading to molar mass build-up.

4. Conclusions

Hyperbranched aromatic polyesters with phenolic end groups were synthesized using the $A_2 + B_3$ and AB_2 approaches. The

$A_2 + B_3$ hb polyesters were prepared by both, solution and melt polymerization. The influence of different monomer ratios (A_2:B_3) on the properties of the resulting $A_2 + B_3$ hb polymers was studied.

In solution polymerization of the A_2 and B_3 monomers, TCl and THPE respectively, a strong dependence of yield and molecular weight of the resulting hb polymers as well as gelation on the monomer ratio (A_2:B_3) were observed. With approaching the stoichiometric ratio of the functionalities the molecular weight of resulting hb polymers were increased and as a consequence also T_g and DB. However, at the same time, gelation could no longer be avoided when high molar mass products were aimed for and with higher monomer concentration of the reaction solution gelation appeared more likely.

The results of TGA investigations indicated a generally high thermal stability of the $A_2 + B_3$ hb polyesters from solution polymerization. Polymerization with lower A_2 monomer ratio, however, resulted in hb polymers with higher amount of oligomeric species which lowered the whole thermal stability of these $A_2 + B_3$ hb polymers since as first step of the thermal degradation phenol evolution from the terminal THPE groups was identified. The kinetic investigation on the solution polymerization of $A_2 + B_3$ monomers (1:1) indicated that the polymerization was almost finished (93% of B_3 conversion) within two hours suggesting an easy and fast synthesis of hb polymer with high T_g (199–268 °C). Generally, the synthesis of $A_2 + B_3$ hb polyester by solution polymerization has the advantage of very mild synthetic conditions and the use of low cost commercially available monomers.

In the melt polymerization of TCl and TMS-THPE, also a dependence of DB and molar mass on monomer ratios (A_2:B_3) was found. In general, the hb polymers synthesized by melt polymerization exhibited lower yields, DB, molar masses than those of the hb polyesters produced from solution polymerization with the same monomer ratio, however, no gelation was observed. Most probably, volatilization of the A_2 monomer (TCl) during the melt polymerization and thus changes in the monomer ratio was the reason for this difference.

Furthermore, comparison of the $A_2 + B_3$ hb polyesters with the AB_2 hb polyester was performed. First, fully soluble high molar mass products can be obtained by the AB_2 approach with no danger of gelation. The AB_2 products possess a higher DB and comparable T_g as the $A_2 + B_3$ products but a lower thermal stability due to higher amount of terminal phenol groups.

The melt rheology of both, the AB_2 hb polyester and the $A_2 + B_3$ (3:4) hb polyester from solution polymerization, exhibited a shear thinning behavior, which is characteristic for hb polymers with phenolic or carboxylic end groups. A small deviation of the complex viscosity of the $A_2 + B_3$ (3:4) hb polyester may be caused by post-polymerization molar mass build-up during the high temperature processing. $A_2 + B_3$ (3:4) hb polyester exhibited a predominately viscous behavior ($G'' > G'$), while the AB_2 hb polyester acted as completely elastic material ($G'' < G'$).

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