Molar mass distribution of a commercial aliphatic hyperbranched polyester based on 2,2-bis(methylol)propionic acid

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Abstract

The determination of absolute molar mass averages (MMA) and molar mass distribution (MMD) of the fourth generation hyperbranched polyester Boltorn H40 (Perstorp Specialty Chemicals AB), synthesized from 2,2-bis(methylol)propionic acid (bis-MPA) as the AB_2 monomer and ethoxylated pentaerythritol as the B_4 core molecule was studied in dependence on the type of solvent, preparation procedure and solution concentration. Due to a large number of polar hydroxyl groups, ester, and also some residual carboxyl groups, a very stable H-bond network is formed at room temperature, that can-not be completely disrupted by dissolving the sample in solvents such as tetrahydrofuran (THF), *N,N*-dimethylacetamide (DMAc), a mixture of THF and methanol (9:1, v/v), and a solution of 0.7% LiBr in DMAc. The H-bonds between the polar groups break down completely and the dissolution of Boltorn H40 on the molecular level is achieved only when the sample is thermally pretreated at a minimum 140 °C for at least 20 min prior to dissolution in solvents THF/methanol or LiBr/DMAc. Thus, determined MMA and molar mass distribution (MMD) of Boltorn H40 are independent on the kind of the solvent and solution concentration.
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Keywords: Molar mass distribution; Light scattering; Molar mass averages; Hyperbranched polyester

1. Introduction

Hyperbranched polymers, like dendrimers, are part of the family of multibranched or dendritic polymers. Contrary to linear polymers, dendritic polymers contain a large number of branching points and functional end groups, which result in their unique physical and chemical properties [1–6]. Dendrimers are well-defined, highly branched macromolecules that radiate from a central core and are synthesized tediously through a stepwise, repetitive reaction sequence that guarantees complete shells for each generation. Dendrimers are thus monodisperse polymers [7]. On the contrary, hyperbranched polymers are more easily made on a large scale in a one pot synthetic step via step-growth polycondensation, self-condensing vinyl or ring-opening polymerization [8]. Hyperbranched polymers are considered irregular analogues of dendrimers since they contain partially reacted linear repeat units in addition to fully reacted (dendritic) and unreacted (terminal) repeat units. Therefore, hyperbranched

polymers have less defined structures than dendrimers and have broader molar mass distributions (MMD).

The physical properties of polymeric materials depend not only on molecular architecture but also on molar mass averages (MMA) and molar mass distribution (MMD). MMA and MMD of highly branched polymers obtained by polycondensation of AB_x monomers depend on conversion, p, as well as monomer functionality, x [9]. At higher conversion, when the reaction approaches completion, the MMD of the product is extremely broad and the polydispersity index (PDI = $\bar{M}_w/\bar{M}_n$) is predicted to approach infinity. Significant deviations from the expected molar mass growth are caused by side reactions, e.g. intramolecular reaction of A and B groups (cyclization) and intra- or inter-molecular reaction of a B group with another B group, which compete with the desired intermolecular reaction of A and B groups.

The MMA of a hyperbranched polymer can be controlled and PDI considerable reduced by the addition of a small amount of multifunctional core molecules, B_f, to the reaction system [10,11]. This largely prevents the coupling of the polymeric species itself. The most effective procedure is to slowly add AB_x monomers to the core molecules in solution ("core dilution/slow addition technique") [12]. The MMA of

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the resulting polymer is controlled by a monomer/core ratio and the PDI by the functionality f of the core molecule B_f. In the ideal case, PDI is defined by $PDI = 1 + (x - 1)/f$. The most important side reaction in the core dilution/slow addition procedure is a deactivation of the A group of the AB_x monomer leading to hyperbranched structures without core molecules [12,20]. This side reaction increases the PDI of the final product.

The control over the MMA and MMD of hyperbranched polymer by the use of a multifunctional core moiety in the polycondensation of AB_2 monomers has been exemplified by the synthesis of hyperbranched aliphatic polyesters from 2,2-bis(methylol)propionic acid (bis-MPA) and various core molecules, either tris(methylol)propane or ethoxylated pentaerythritol [13–15]. Hult reported a pseudo-one-step reaction where stoichiometric amounts of bis-MPA monomer, corresponding to each generation, were added successively to the core molecules in the bulk under acidic catalysis. MMA and MMD of such obtained poly(bis-MPA) polyesters are also influenced by possible side reactions such as the intramolecular reaction of carboxyl and hydroxyl groups, and two hydroxyl groups into an ether bond. These side reactions lead to cyclic structures [16–18]. The importance of the first side reaction in the synthesis of poly(bis-MPA) hyperbranched polyesters was studied by comparison of experimentally determined number-average molar mass, $\bar{M}_n$, by vapor pressure osmometry (VPO) and that calculated from ^{1}H NMR spectra. Cyclization as a side reaction reduces the average degree of polymerization of the final product. Etherification can also occur intermolecularly leading to the formation of cross-linked structures and subsequently resulting in the gelation of the product [17].

The literature data on the molar mass characterization of poly(bis-MPA) hyperbranched polyesters comprise mainly their relative MMA determined by SEC under various chromatographic conditions (solvent, temperature, polymer standards for column calibration) [13–17]. Since the hydrodynamic volume of a dendritic polymer is smaller than that of its linear analog of the same molar mass, the reported relative MMA of these polyesters are often lower than expected. In addition, the SEC results can be affected by the interactions of a large number of polar functional groups with the column packing, which is especially the case for the solvent THF [13]. Another problem in MMA determination of poly(bis-MPA) hyperbranched polyesters is their strong tendency to associate due to the strong intermolecular interactions between polar end-hydroxyl groups even in polar solvents such as *N,N*-dimethylformamide (DMF) [19]. The absolute $\bar{M}_n$ of these polyesters determined by VPO were reported on only recently [16]. The $\bar{M}_n$ of poly(bis-MPA)s have also been calculated from ^{1}H NMR spectra [16,20]. The absolute MMA of Boltorn H40 and its fractions have been reported in our previous paper [20].

This work focuses on the difficulties encountered in molar mass determination of a commercial fourth generation hyperbranched polyester synthesized from bis-MPA and ethoxylated pentaerythritol (Boltorn H40, Perstorp) in tetrahydrofuran (THF) and *N,N*-dimethylacetamide (DMAc) as the most widely used solvents for this kinds of samples. In addition, it describes a development of the sample preparation procedure assisted by size exclusion chromatography coupled to a multi-angle laser light scattering photometer (SEC-MALS), differential scanning calorimetry (DSC), NMR and FT-IR techniques, that allows dissolution of the sample on a molecular level. We studied sample molar mass distribution by using SEC-MALS in THF, a mixture of THF and methanol (THF/MeOH = 9:1, v/v), DMAc, and in a 0.7% solution of LiBr in DMAc. We considered the type of solvent, procedure for solution preparation, and solution concentration. The developed procedure can also be useful for the molar mass determination of other hydroxy-functional hyperbranched polymers.

2. Experimental

2.1. Sample

Boltorn[TM] H40 (Scheme 1) is a commercially available fourth generation hydroxy-functional hyperbranched polyester synthesized from 2,2-bis(methylol)propionic acid (bis-MPA) as the AB_2 monomer and ethoxylated pentaerythritol (PP50) as the B_4 core molecule (Perstorp Specialty Chemicals AB). Our sample denotation is H40. H40 as an ideal dendrimer would theoretically have 64 primary hydroxyl groups and a molar mass of 7,316 g mol^{-1}. It is delivered in pellets and is an amorphous solid at room temper-
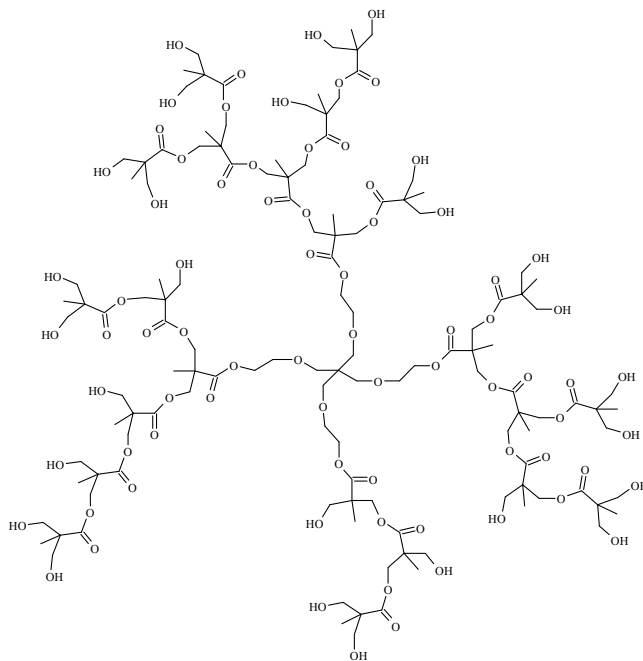
Scheme 1. Chemical structure of hyperbranched polyester based on bis-MPA and the PP50 core molecule.

ature. Its specifications are the following: hydroxyl number is 470–500 mg KOH g^{-1}, acid number is 7–11 mg KOH g^{-1}, $\bar{M}_w$ = 5100 g mol^{-1} and PDI ($\bar{M}_w/\bar{M}_n = 1.8$) (determined by SEC in 0.2% LiBr/DMF using polyethylene glycol standards), viscosity (110 °C, 30 s^{-1}) is 110 Pa s, and the glass transition temperature, T_g, is 40 °C.

2.2. Characterization

The SEC-MALS measurements were performed at 25 °C using a Hewlett Packard pump series 1100 coupled to a Dawn-DSP laser photometer equipped with an He–Ne laser ($\lambda_0 = 633$ nm) and to an Optilab-DSP interferometric refractometer (DR) (both instruments are from Wyatt Technology Corp., USA). Separations were carried out using: (i) a PLgel 5 μm Mixed-D column (300 mm length and 7.5 mm i.d.) with a precolumn in tetrahydrofuran (THF, Fluka) and DMAc with a 0.7% concentration of LiBr (Aldrich) added, and (ii) two Mixed-D columns (Polymer Laboratories Ltd.) with a precolumn in DMAc (Aldrich) and a mixture of THF and methanol (MeOH, Merck) in a volume ratio of 9:1. The PLgel Mixed-D column contains a mixture of individual pore size materials that cover a range of molar masses from 200 g mol^{-1} to 400,000 g mol^{-1}. The nominal flow rate of all eluents was 0.9 ml min^{-1}. The mass of the hyperbranched polyester injected onto the column was typically (1–3) × 10^{-3} g, whereas the solution concentration was (1–3) × 10^{-2} g ml^{-1}. The sample dissolution procedure is described in the text below. The calculation of $\bar{M}_w$ from MALS requires a sample specific refractive index increment (dn/dc), which was determined from the DRI response assuming a sample mass recovery from the column of 100%. Data acquisition and evaluation utilized Astra 4.73.04 software (Wyatt Technology Corp.). Since a MALS detector is not particularly sensitive toward low molar mass species, the sample molar mass averages were recalculated using Corona 1.40 software (Wyatt Technology Corp.), where the scattered data points at the end of the chromatogram were fitted by the linear regression [21].

The dn/dc of H40 in THF is 0.078 ml g^{-1}. It was determined separately on an Optilab-DSP refractometer at the same wavelength as operating the Dawn-DSP laser photometer ($\lambda_0 = 633$ nm). Six solutions with a concentration ranging from 0.5 × 10^{-3} to 8 × 10^{-3} g ml^{-1} were prepared. Data acquisition and evaluation utilized DNDC 5.00 software.

The ^{1}H NMR spectra were recorded on a Varian Unity Inova 300 MHz spectrometer using THF-d_8, DMAc-d_9, methanol-d_4, THF-d_8/methanol-d_4 mixture, LiBr/DMAc-d_9, and dimethylsulfoxyde DMSO-d_6 as a solvent. Tetramethylsilane (TMS) was used as an internal reference. Integrals in the ^{1}H NMR spectra were obtained using a solution of 0.5% concentration at room temperature (°C) (a relaxation delay of 20 s, an acq. time of 5 s, and up to 500 repetitions).

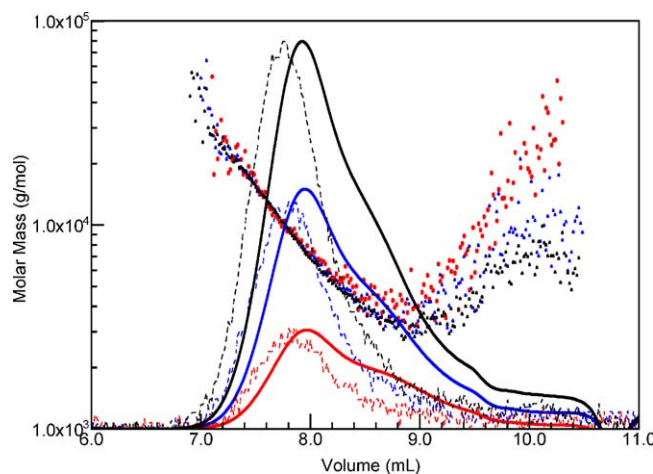DSC measurements were made using a Pyris 1 Perkin-Elmer DSC apparatus with Al pans at a heating rate of 10 °C min^{-1}.

Fig. 1. SEC-MALS chromatograms ((—) DRI response, (- - -) LS response at 90° angle), and molar mass vs. elution volume curves for Boltorn H40 in THF at three different concentrations injected (see Table 1, injection volume = 100 μl).

3. Results and discussion

3.1. Solvent tetrahydrofuran (THF)

The SEC curves of H40 in low polarity THF at three different solution concentrations are asymmetrical, indicating broad molar mass distribution of the sample (Fig. 1). The response of the DRI detector (Fig. 1) and the dn/dc value (Table 1) increase with increasing solution concentration; the dn/dc was determined at each solution concentration assuming a 100% sample mass recovery from the column. At constant dn/dc, which was determined separately by interferometric refractometer, the sample MMA increase, whereas the calculated mass of the sample recovered from the column decreases with decreasing solution concentration (Table 1). The molar mass versus elution volume plots (Fig. 1) at three solution concentrations and the constant dn/dc overlap up to an elution volume of about 8.3 ml. Above this elution volume the curves deviate, indicating the elution of higher molar mass species at larger elution volumes. At a given elution volume, the molar mass of the eluted species increases with decreas-

Table 1
SEC-MALS results for Boltorn H40 in THF

Injected mass (g)	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	dn/dc (ml g^{-1})	Mass recovery (%)
Assuming 100% sample mass recovery from the column					
0.492 × 10^{-3}	12,070	9,440	1.28	0.051	100
1.004 × 10^{-3}	9,610	7,460	1.29	0.060	100
1.506 × 10^{-3}	8,620	6,570	1.31	0.065	100
dn/dc = 0.078 ml g^{-1}					
0.492 × 10^{-3}	7,910	6,180	1.28	0.078	65.5
1.004 × 10^{-3}	7,390	5,740	1.29	0.078	76.9
1.506 × 10^{-3}	7,170	5,460	1.31	0.078	83.2
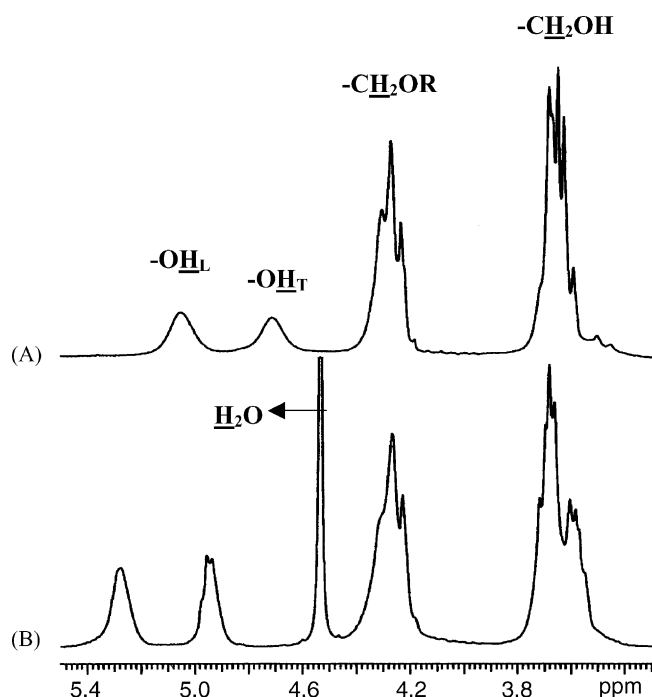
Fig. 2. ^{1}H NMR spectra of Boltorn H40 recorded in (A) DMAc-d_9 and (B) LiBr/DMAc-d_9 solutions.

Fig. 3. ^{1}H NMR spectra of Boltorn H40 recorded in (A) THF-d_8, (B) THF-d_8/MeOH-d_4, and (C) MeOH-d_4 solutions.

ing solution concentration (Fig. 1). These results suggest that the elution of H40 in THF is governed not only by size-exclusion mechanism, but also by adsorption, which is irreversible for low molar mass species. Therefore, the recovered mass of the sample was lower than that injected onto the column and consequently, the reproducibility of the measurements was poor. The relative amount of the sample retained on the column increased with decreasing solution concentration (Table 1), which is in opposition to the expected enhanced solubility of the sample at lower concentrations. This phenomenon can be explained by the saturation of available sites on the column packing, which are most probably of the type causing the interaction with carboxyl groups. Since the retained species having free carboxyl groups are mainly hyperbranched macromolecules without the core molecule and having lower molar masses than macromolecules with a core molecule [20], the determined MMA of the sample increase with decreasing solution concentration.

3.2. Solvent N,N-dimethylacetamide (DMAc)

In high polarity DMAc, the solubility of the sample is improved compared to that in THF, since DMAc better solvates the polar groups of H40. This is indicated by the downfield shift of proton signals of hydroxyl groups in the terminal and linear repeat units of H40 in ^{1}H NMR spectra recorded in DMAc solution (Figs. 2A and 3A). However, the sample MMD is extremely broad and MMA are highly overestimated [20].
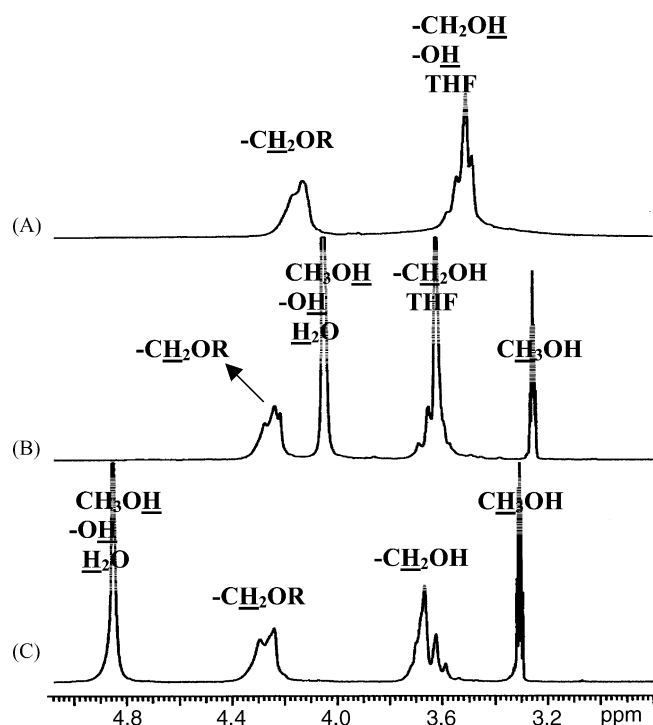
3.3. Solvents tetrahydrofuran/methanol (THF/MeOH = 9:1, v/v) and 0.7% LiBr/DMAc

In order to dissolve the sample on a molecular level and prevent adsorption onto the column packing, a small amount of methanol (10 vol.%) was added to THF, and LiBr (0.7%) to DMAc, respectively. Methanol, as a solvent of higher polarity than THF, preferentially solvates polar hydroxyl and carboxyl groups of H40, whereas Br$^-$ and [Li(DMAc)$_n$]$^+$ ions form complexes with these groups, which was indicated also by the ^{1}H NMR spectroscopy. The protons of hydroxyl groups in terminal and linear repeat units of H40 in DMAc resonate at 4.71 and 5.05 ppm (Fig. 2A), like in DMSO [20]. After the addition of LiBr, these two signals shifted downfield to 4.95 and 5.28 ppm as a consequence of complex formation (Fig. 2B). In THF, the –OH protons resonate at the same chemical shift as the –CH_2OH protons of H40 and –CH_2– protons of THF (between 3.2 and 3.8 ppm, Fig. 3A). This was inferred from the comparison of the integrals for the protons of H40 individual groups (–CH_3, –CH_2OR, –CH_2OH, –OH) in DMSO [20], DMAc, and THF. By the addition of methanol to THF the protons of H40 –OH groups shift to 4.05 ppm. This signal overlaps with the signal of CH$_3$OH groups (Fig. 3B). In pure methanol, both signals appear at 4.85 ppm (Fig. 3C).

By the addition of methanol to THF and LiBr to DMAc the intermolecular H–bonds between polar groups of H40 are disrupted to a large extent and the possibility of aggregation is considerable reduced. Nevertheless, a LS detector
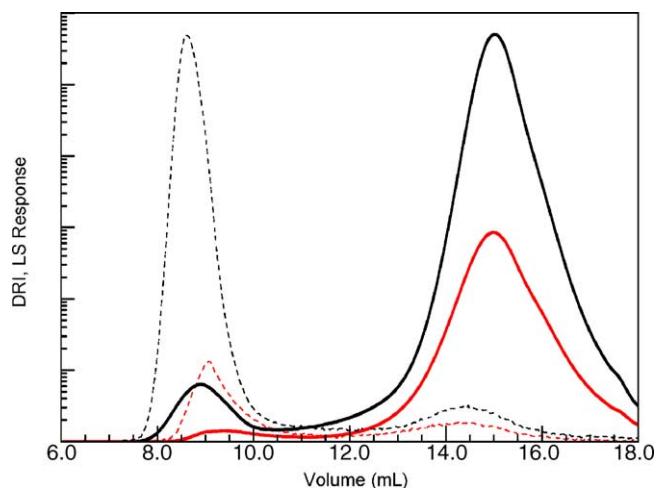
Fig. 4. SEC-MALS chromatograms ((—) DRI response, (- - -) LS response at 90° angle), of Boltorn H40 in THF/MeOH at two different concentrations (see Table 2, injection volume = 100 μl).

Table 2
SEC-MALS results for Boltorn H40 in THF/MeOH (9:1, v/v) and 0.7% LiBr/DMAc

Injected mass (g)	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	dn/dc (ml g^{-1})
THF/MeOH (9:1, v/v)				
1.004×10^{-3}	21,200	5,600	3.78	0.074
2.064×10^{-3}	36,600	5,800	6.31	0.074
0.7% LiBr/DMAc				
1.050×10^{-3}	9,250	4,660	1.98	0.065
2.012×10^{-3}	9,670	4,680	2.07	0.065

MMA were calculated assuming complete sample mass recovery from the column.

still indicates minute amounts of aggregated species in both solutions, that have eluted at lower elution volumes and are barely detected by DRI (Figs. 4 and 5). As in DMAc, the sample dn/dc values do not change in THF/methanol and LiBr/DMAc solutions, whereas the sample MMA increase with increasing solution concentration (Table 2). These results indicate complete sample mass recovery from the column and increasing degree of aggregation with increasing solution concentration.

The obtained SEC-MALS results reveal that the Boltorn H40 forms a very stable H-bond network at room temperature, that can-not be completely disrupted merely by dissolving the sample in the above mentioned solvents. The H-bond network, formed from a large number of hydroxyl and ester groups, as well as some residual carboxyl groups, was investigated by FT-IR thermal analysis [22] and DSC
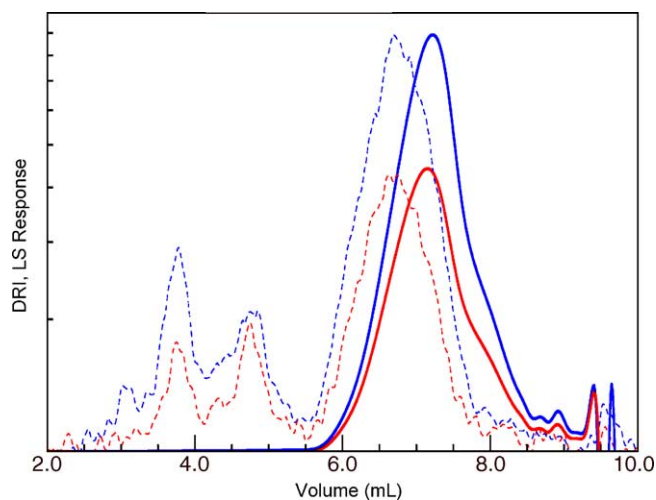
measurements. The DSC trace of H40 showed T_g at around 33 °C and an endothermic peak between 60 and 140 °C with the apex at 80 °C (Fig. 6). This peak was ascribed to the fusion of ordered domains of H-bonded hydroxyl groups. Namely, the endothermic peak was accompanied by a pronounced frequency change in the OH stretching band observed in the FT-IR thermal analysis. A detailed analysis of FT-IR spectral parameters (frequency, bandwidth, band area and band shape) of all possible proton acceptor groups suggests that this frequency jump is mainly a consequence of the weakening of H-bonds between hydroxyl groups [22].

Considering DSC and FT-IR results we presumed that H-bonds between functional groups of the Boltorn H40 polyester could be disrupted by heating the sample to 140 °C [22]. The minimum time for breaking the H-bond network successfully was 20 min. Therefore, the sample was thermally pretreated at 140 °C for 20 min before it was dissolved in THF/methanol (9:1) or 0.7% LiBr/DMAc. The obtained non-H-bonded state was frozen by submerging the sample into liquid N$_2$ and the solvent was added to the frozen sample. After complete dissolution of the sample, the solutions were kept at 0 °C in refrigerator, since the association was found to be a reversible process at room temperature, especially in THF/methanol mixture. For this reason and in order to completely prevent the association via
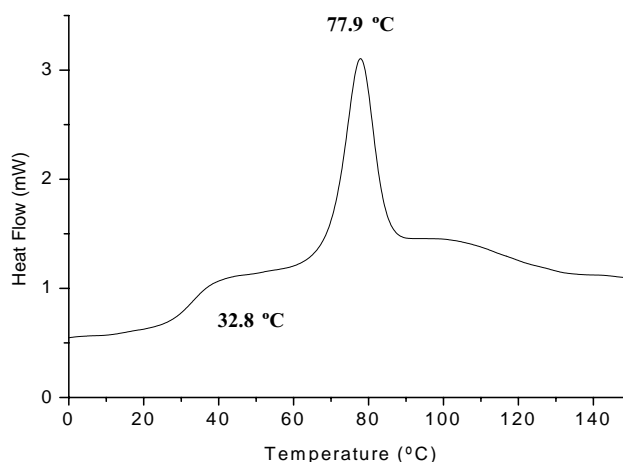

Fig. 5. SEC-MALS chromatograms ((—) DRI response, (- - -) LS response at 90° angle), of Boltorn H40 in LiBr/DMAc at two different concentrations injected (see Table 2, injection volume = 100 μl).

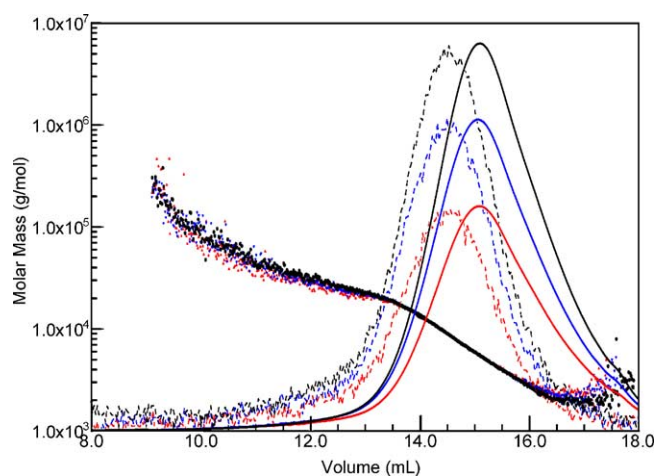Fig. 6. Normalized DSC trace of Boltorn H40 (first heating scan).

Fig. 7. SEC-MALS chromatograms ((—) DRI response, (- - -) LS response at 90° angle), and molar mass vs. elution volume curves for thermally pretreated (140 °C, 20 min) Boltorn H40 in THF/MeOH (9:1, v/v) at three different concentrations injected (see Table 3, injection volume = 100 μl).

hydrogen bonds, the sample was first dissolved in methanol and THF was added to the methanol solution just prior to the SEC-MALS measurements. In this way the obtained MMA of H40 were independent of solution concentration in both solvents (THF/methanol or LiBr/DMAc) indicating dissolution of the sample on a molecular level (Figs. 7 and 8, Table 3). Since a MALS detector is not particularly sensitive toward low molar mass species, which particularly influences the determination of the $\bar{M}_n$ value, the scattered data points at higher elution volumes were fitted using linear regression [20]. The obtained MMA and MMD values for Boltorn H40 are comparable in both solvents; $\bar{M}_w$ is 6860 g mol^{-1} in THF/MeOH and 6640 g mol^{-1} in LiBr/DMAc, and $\bar{M}_n$ is 2,630 g mol^{-1} in THF/MeOH and 2,580 g mol^{-1} in LiBr/DMAc. The sample PDI (2.6) is higher than it would be theoretically (1.25) as a con-
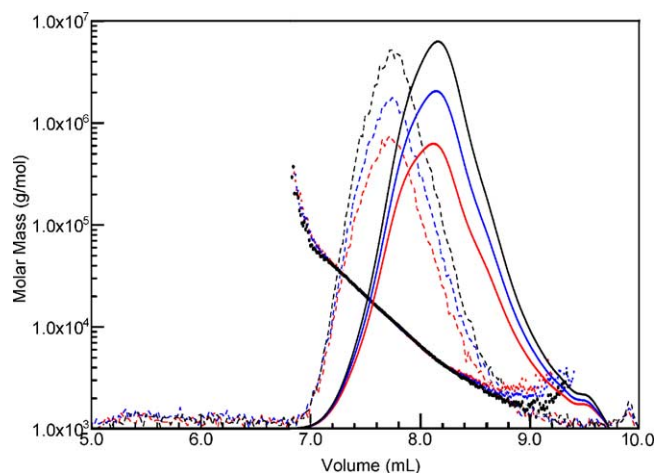

Fig. 8. SEC-MALS chromatograms ((—) DRI response, (- - -) LS response at 90° angle), and molar mass vs. elution volume curves for thermally pretreated (140 °C, 20 min) Boltorn H40 in 0.7% LiBr/DMAc at three different concentrations injected (see Table 3, injection volume = 100 μl).

Table 3
SEC-MALS results for thermally pretreated (140 °C, 20 min) Boltorn H40 in THF/MeOH (9:1, v/v) and 0.7% LiBr/DMAc fitted by the Corona software

Solvent system	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w / \bar{M}_n$	dn/dc (ml g^{-1})
THF/MeOH (9:1, v/v)	6,860	2,630	2.61	0.074
LiBr/DMAc (0.7%)	6,640	2,580	2.57	0.065

MMA were calculated assuming complete sample mass recovery from the column. $\bar{M}_w$, $\bar{M}_n$, $\bar{M}_w / \bar{M}_n$ are average values obtained at three different solution concentrations [20].

sequence of a deactivation of bis-MPA carboxyl groups [20].

Acknowledgements

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