

Properties of aliphatic hyperbranched polyesters in dilute solutions

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Abstract: The results of an investigation of the influence of the synthesis procedure, number of pseudo generations and degree of branching of hydroxy-functional aliphatic hyperbranched polyesters (AHBP) on the values of limiting viscosity number, $[\eta]$, hydrodynamic radius, R_{η} , molar mass and polydispersity index, Q , are presented in this paper. Two series of AHBP, synthesized from 2,2-bis(hydroxymethyl)propionic acid and di-trimethylolpropane using a pseudo-one-step and a one-step procedure were investigated. The obtained results show that the values of $[\eta]$ and R_{η} for all examined samples are the highest in a 0.7 mass % solution of LiCl in *N,N*-dimethylacetamide (LiCl/DMAc), which indicates that this solvent is the best from the investigated ones. The values of $[\eta]$ in *N*-methyl-2-pyrrolidinone (NMP) increased up to the sixth pseudo generation, after which a slight decrease occurred as the consequence of the presence of side-reaction products, formed during the synthesis. The appearance of these side-reaction products was also confirmed from the characteristic GPC chromatograms. For the samples of AHBP synthesized using the pseudo-one-step procedure, a good linear dependence between $\log [\eta]$ and $\log M_w$ was obtained up to the fifth pseudo generation, when LiCl/DMAc, NMP and DMAc were used as solvents. The values of the “shrinking” factor, g' , were calculated for all investigated AHBPs.

Keywords: aliphatic hyperbranched polyesters, dilute solutions, limiting viscosity number, GPC.

INTRODUCTION

The scientific importance of dendritic polymers, *i.e.*, dendrimers (ideally branched) and hyperbranched polymers (non-ideally branched) has been proved over the last two decades through the significant number of publications.¹ The results obtained during investigation of the structure and properties of these specific polymers have made great contribution to their growing fields of applica-

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tion.² Dendritic polymers are often used in solution and therefore special attention has been devoted to the research of their behaviour in dilute and concentrated solutions.^{3–12} It was shown that these polymers have lower limiting viscosity number, $[\eta]$, values than the analogue linear polymers of the same molar mass and chemical composition, due to the presence of highly branched macromolecules. In addition, the logarithm of the limiting viscosity number of linear polymers increases linearly with increasing logarithm of molar mass, while for dendrimers a maximum is usually observed in this relationship.^{3–5} Beside experimental work, there are also different simulation methods which predict this behaviour of dendrimers in dilute solutions.⁶ This specific behaviour of dendrimers in dilute solutions can be explained by the fact that their hydrodynamic radius linearly increases with increasing number of generation, n , while their molar mass grows as according to 2^n (the factor “2” comes from the assumed dendrimer functionality).

Concerning the dependence between $\log [\eta]$ and $\log M$ for hyperbranched polymers, different results can be found in the literature. Fréchet *et al.* suggested that $[\eta]$ always increases with the molar mass but slower than for linear polymers.⁷ However, the dependence $\log [\eta] = f(\log M)$ of poly(amidoamine) hyperbranched polymers was shown to have the same trend as for dendrimers.⁸ Published simulations of the behaviour of hyperbranched polymers in solution predict the presence of a maximum in the dependence between $\log [\eta]$ and $\log M$, but this maximum comes at a higher number of generations than for the equivalent dendrimers and it disappears when the degree of branching is lower than 0.3.^{9,10} On the other hand, for several hyperbranched polymers, this maximum was not observed.^{1g,11}

In this study, the influence of the synthesis procedure (pseudo-one-step and one-step), number of pseudo generations and degree of branching of hydroxy-functional aliphatic hyperbranched polyesters (AHBP) synthesized from 2,2-*bis*(hydroxymethyl)propionic acid (*bis*-MPA) and di-trimethylolpropane (DiTMP) on the limiting viscosity number, dimensions of the macromolecules in solution, R_η , molar mass and polydispersity index, Q , was investigated. The obtained results are compared with appropriate experimental results presented in the literature.

EXPERIMENTAL

Materials

Two series of hydroxy-functional aliphatic hyperbranched polyesters were synthesized *via* an acid-catalyzed polyesterification reaction starting from *bis*-MPA (Aldrich), as the AB₂ monomer, and DiTMP (Fluka Chemika), as the tetrafunctional core molecule,^{1h} methanesulphonic acid (Aldrich) was used as the catalyst. Samples of series I of the second (AHBP-2I), third (AHBP-3I), fourth (AHBP-4I), fifth (AHBP-5I), sixth (AHBP-6I), eighth (AHBP-8I) and tenth (AHBP-10I) pseudo generation were synthesized using a pseudo-one-step procedure. On the other hand, samples of series II of the fourth (AHBP-4II), sixth (AHBP-6II) and eighth (AHBP-8II) pseudo generation were synthesized using a one-step procedure. In this work, three commercially available AHBPs (Boltorn®) of the second (BH-2), third (BH-3) and fourth (BH-4) pseudo generation were also in-

vestigated. These AHBP were supplied by Perstorp (Specialty Chemicals AB, Sweden). According to the supplier's data, the commercial AHBPs were synthesized *via* a pseudo-one-step procedure from *bis*-MPA as monomer and a tetrafunctional ethoxylated pentaerythritol (PP50) core. All other chemicals were obtained from Aldrich and used as received, without further purification.

Characterization

^{13}C -NMR spectra of the samples were recorded on a Bruker (250 MHz) NMR spectrometer at room temperature using deuterated dimethylsulfoxide ($\text{DMSO-}d_6$) as the solvent. The degree of branching (DB) was calculated from the values obtained by integration of the appropriate peaks, corresponding to the dendritic, linear and terminal units and using the equation developed by Fréchet:¹³

$$DB = (n_D + n_T) / (n_D + n_L + n_T) \quad (1)$$

where n_D , n_T and n_L represent the number of dendritic, terminal and linear units, respectively.

Vapour pressure osmometry (VPO) of the synthesized and commercial samples was performed using a Knauer vapour pressure osmometer. The measurements were realised in *N,N*-dimethylformamide as the solvent at 90 °C. Benzil was used for the calibration.

Determination of the molar mass distribution of the AHBPs was performed by the GPC technique using a Spectra-Physics chromatograph equipped with Rheodyne universal injector and Spectra-Physics differential refractometer as detector. The separation was achieved across a set of two gel columns (MZGPC columns) with porosities of 1000 Å. Tetrahydrofuran (THF) was used as the eluent at a nominal flow rate of 1.0 cm³ min⁻¹. The quantity of injected polymer was 100 µl ($c \approx 20$ g l⁻¹) and the measurements were performed at 25 °C. The molar mass characteristics of the polymers were calculated from a polystyrene calibration curve, constructed with narrow molar mass distribution polystyrene standards (Polymer Standards Service), using Chrom Gate 3.1.4 software (Knauer).

The viscosity measurements of dilute solutions of the AHBPs in different solvents were performed in an Ubbelohde capillary viscometer (Schott, capillary sizes O_a and I) using an automatic timer (Schott AVS 300), at 25±0.1 °C. The limiting viscosity number and Huggins constant, k_H , of the samples were determined graphically by extrapolation of the η_{sp}/c values (determined at five different concentrations) to infinite dilution using the Huggins equation.¹⁴

Seven samples of self-synthesized and Boltorn[®] hyperbranched polyesters (AHBP-3I, AHBP-4I, AHBP-6I, AHBP-8I, AHBP-10I, BH-3 and BH-4) were fractionated using the precipitation fractionation method¹⁵ from a solvent/non-solvent (acetone/*n*-hexane) mixture to obtain three fractions of each sample. All obtained fractions were dried in a vacuum oven to remove the volatile materials.

RESULTS AND DISCUSSION

For all AHBP samples investigated in this work, the value of the number average molar mass was determined using vapour pressure osmometry, $(M_n)_{\text{VPO}}$, while the DB value was calculated according to Fréchet.¹³ These values together with theoretical number of pseudo generation, n_{theor} , and theoretical molar mass, M_{theor} , are listed in Table I.

From the parameters listed in Table I, it can be seen that the molar mass, $(M_n)_{\text{VPO}}$, increased only up to the sixth pseudo generation and simultaneously was much lower than the theoretical value. The reason for this specific behaviour is the occurrence of side reactions during the synthesis of these polyesters.^{1h} The extent of undesired reactions increased with increasing generation number. For all the investigated AHBPs, the values of the degree of branching slightly de-

creased with increasing theoretical number of pseudo generations. Moreover, for the samples of the second series AHBP-4II, AHBP-6II and AHBP-8II, the *DB* values were lower than for the corresponding samples of the first series, indicating a slight influence of the synthesis procedure on the degree of branching.

TABLE I. Values of the theoretical number of pseudo generation, n_{theor} , theoretical molar mass, M_{theor} , number average molar mass determined by VPO, $(M_n)_{\text{VPO}}$ and degree of branching, *DB*, of the investigated AHBPs

Sample	n_{theor}	$M_{\text{theor}} / \text{g mol}^{-1}$	$(M_n)_{\text{VPO}}^{\text{a}} / \text{g mol}^{-1}$	<i>DB</i>
AHBP-2I	2	1642	–	0.47 ^a
AHBP-3I	3	3498	2027	0.45 ^a
AHBP-4I	4	7210	2819	0.44 ^a
AHBP-5I	5	14634	3044	0.45 ^a
AHBP-6I	6	29482	3575	0.43 ^a
AHBP-8I	8	118570	3571	0.43 ^a
AHBP-10I	10	474922	3552	0.42 ^a
AHBP-4II	4	7210	5415	0.42 ^a
AHBP-6II	6	29482	–	0.43 ^a
AHBP-8II	8	118570	3284	0.37 ^a
BH-2	2	1747	1343	0.43 ^b
BH-3	3	3604	3081	0.42 ^b
BH-4	4	7316	2716	0.40 ^b

^aResults for $(M_n)_{\text{VPO}}$, and *DB* are presented in Ref. 1h; ^bdata of Luciani *et al.*¹⁶

Limiting viscosity number and hydrodynamic radius of the AHBP in different solvents

Since the polyesters investigated in this work had a large number of free OH groups, it is reasonable to expect that the macromolecules of AHBP in solution, similar to poly(vinyl alcohol), would connect with each other through the hydrogen bridges and form aggregates. Investigation of the properties of macromolecules in solution becomes much more difficult when spontaneous aggregate formation occurs. Žagar *et al.*¹⁷ reported that samples of AHBP thermally pre-treated for 20 min at 140 °C do not form aggregates at room temperature in a 0.7 mass % solution of LiBr in N,N-dimethylacetamide (LiBr/DMAc) and in a mixture of tetrahydrofuran (THF) and CH₃OH (90:10 by volume) and that these solvents are therefore suitable for the investigation of the properties AHBPs in solution. Instead, LiBr/DMAc, a 0.7 mass % solution of LiCl in DMAc (LiCl/DMAc) was used for the determination of $[\eta]$ in this work. In addition to this solvent, viscosity measurements were also performed in *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), THF and in a mixture THF/CH₃OH (90:10 by volume).

As examples of the determination of $[\eta]$, the dependences of η_{sp}/c vs. *c* for different AHBP of series I in NMP and for the sample AHBP-8I in the employed solvents are presented in Figs. 1a and 1b, respectively. Since a linear relationship

was obtained between η_{sp}/c and c in all the employed solvents, it can be concluded that no aggregation occurred in the investigated concentration range or that the shear stress which developed in the capillary of the viscosimeter was high enough to lead to the rupture of the intermolecular hydrogen bonds present in the aggregates formed in the static solution.

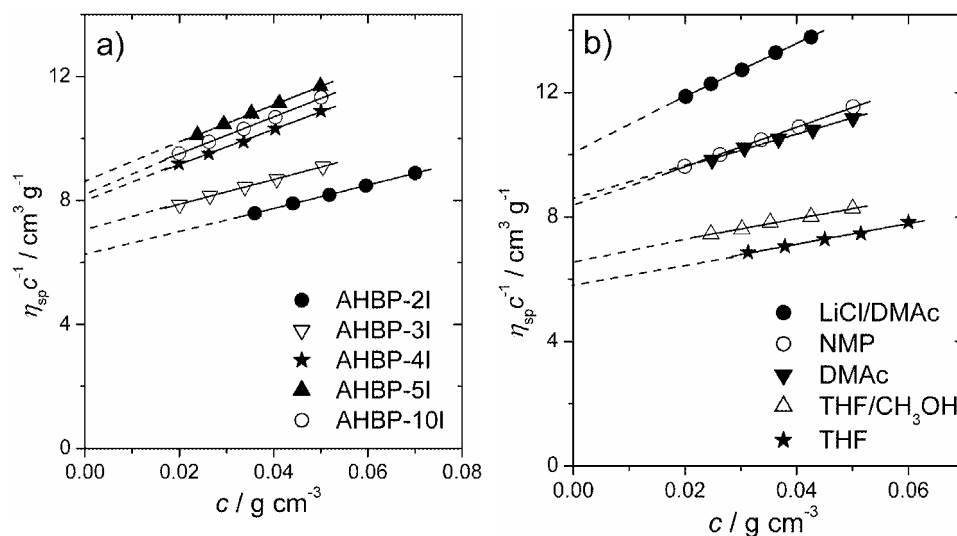


Fig 1. Dependence of η_{sp}/c versus c for a) different AHBPs in NMP and b) for the sample AHBP-8I in different solvents, at 25 °C.

The values of $[\eta]$ were determined for all the examined AHBPs in the mentioned solvents at 25 °C and they are listed in Table II. It should be mentioned that the samples of AHBP were not thermally pre-treated prior to the viscosity measurements.

The dependence of the $[\eta]$ values for the AHBPs from series I in LiCl/DMAc vs. $[\eta]$ of the same samples in NMP is presented in Fig. 2. As all the experimentally determined points fall on one linear plot, it can be concluded that value of $[\eta]$ in LiCl/DMAc and NMP for these AHBPs is independent of the number of pseudo generation, *i.e.*, of the molar mass. This indicates that AHBP samples were dissolved on the molecular level under applied experimental conditions and without thermal pre-treatment, *i.e.*, aggregation did not occur.

The value of $[\eta]$, as well as the value of the slope from the linear dependence $\eta_{sp}/c = f(c)$, presented in Fig. 1b, represent a measure of the solvent quality for the investigated polymer. According to these criteria, LiCl/DMAc is the best of the investigated solvents for AHBP, while the other solvents are ordered as follows:

$$[\eta]_{\text{LiCl/DMAc}} > [\eta]_{\text{NMP}} > [\eta]_{\text{DMAc}} > [\eta]_{\text{THF/CH}_3\text{OH}} > [\eta]_{\text{THF}} \quad (2)$$

TABLE II. Values of the limiting viscosity number, $[\eta]$, of the AHBPs determined in different solvents at 25 °C

Sample	$[\eta]_{\text{LiCl/DMAc}}$ $\text{cm}^3 \text{g}^{-1}$	$[\eta]_{\text{NMP}}$ $\text{cm}^3 \text{g}^{-1}$	$[\eta]_{\text{DMAc}}$ $\text{cm}^3 \text{g}^{-1}$	$[\eta]_{\text{THF/CH}_3\text{OH}}$ $\text{cm}^3 \text{g}^{-1}$	$[\eta]_{\text{THF}}$ $\text{cm}^3 \text{g}^{-1}$
AHBP-2I	6.8	6.2	6.4	–	4.0
AHBP-3I	7.9	7.1	6.5	–	4.8
AHBP-4I	9.9	8.0	7.0	6.4	5.6
AHBP-5I	10.8	8.7	7.8	6.4	5.4
AHBP-6I	11.0	8.9	8.3	6.5	5.9
AHBP-8I	10.2	8.3	8.6	6.6	5.8
AHBP-10I	10.0	8.3	8.2	6.4	–
AHBP-4II	–	8.0	–	–	–
AHBP-6II	–	9.2	–	–	–
AHBP-8II	–	9.3	–	–	–
BH-2	7.0	6.0	6.1	–	–
BH-3	9.2	7.4	–	5.5	–
BH-4	10.7	8.6	–	6.7	4.9

In good agreement with this order of solvents is also the solubility parameter, δ , $10^3 (\text{J m}^{-3})^{0.5}$, which for AHBP have the value of 23.0 for LiCl/DMAc, while the solubility parameters for NMP, DMAc, THF/CH₃OH and THF are 23.1, 22.6, 19.7 and 18.6, respectively.¹⁸ The improvement of the solubility of AHBP in the mixture LiCl/DMAc in comparison to pure DMAc is due to the influence of the Li⁺ ions on the rupture, not only of intermolecular, but also intramolecular hydrogen bonds in the AHBP macromolecules, which further leads to the increase of their volume in solution and, consequently, to the increase of their $[\eta]$ value.

From the slope of the linear dependence of η_{sp}/c vs. c for all investigated AHBPs in different solvents, the values of the Huggins constants, k_{H} , were determined. For the samples of the series I in LiCl/DMAc value of k_{H} is 0.65 ± 0.15 , in NMP 0.80 ± 0.20 , in DMAc 1.0 ± 0.3 and in THF/CH₃OH 0.75 ± 0.05 . For AHBP of series II in NMP the value of k_{H} is 0.85 ± 0.15 . For the commercial AHBP, k_{H} is 0.55 ± 0.05 in LiCl/DMAc and 0.80 ± 0.02 in NMP and in the mixture THF/CH₃OH.

The determined values of k_{H} are different and therefore it is possible to use them for the calculation of $[\eta]$ from the Huggins equation by determination of the specific viscosity, η_{sp} , for only one concentration of the solution, but only for the mentioned AHBP samples. For most linear polymers in good solvents, the value of k_{H} is 0.3–0.4 and is independent of the chemical composition of the polymer. Values of k_{H} for the examined AHBPs in various solvents are different from the values for linear polymers due to the specific molecular structure of the AHBPs and presence of a large number of end groups.

The dependence of $[\eta]$ for AHBP in NMP vs. the theoretical number of pseudo generations is presented in Fig. 3. According to these results, an increase of

$[\eta]$ up to the sixth pseudo generation can be observed for the samples of series I, after which the values of $[\eta]$ slightly decrease. A similar observation was made for the AHBP of series II, while for the commercial samples, $[\eta]$ continuously increased, since these samples were examined only from the second up to the fourth pseudo generation. This specific shape of the dependence presented in Fig. 3 for the samples of series I and II is not a consequence of the increase of the macromolecular packing density with increasing pseudo generation, as is predicted by different simulation methods of the behaviour of hyperbranched polymers in solution.^{9,10} The break in the increase of the $[\eta]$ value after the sixth pseudo generation in this case occurs due to the presence of side reaction products in these polymers, which prevent a further increase of the molar mass.^{1h} Samples of the series II have somewhat higher values of $[\eta]$ in NMP than the AHBPs from series I. This is probably a consequence of the slightly lower values of the degree of branching (Table I) and, therefore, higher amounts of linear branches present in the macromolecules of these samples, which further leads to an increase in $[\eta]$. On comparing the $[\eta]$ values obtained in THF/CH₃OH for AHBPs from the fourth up to the tenth pseudo generation, it can be observed that $[\eta]$ is practically constant, *i.e.*, it does not depend on the molar mass. These results indicate that THF/CH₃OH is a poor solvent, probably due to the fact that these AHBP were not thermally pre-treated, as was the case in other studies.^{17,19}

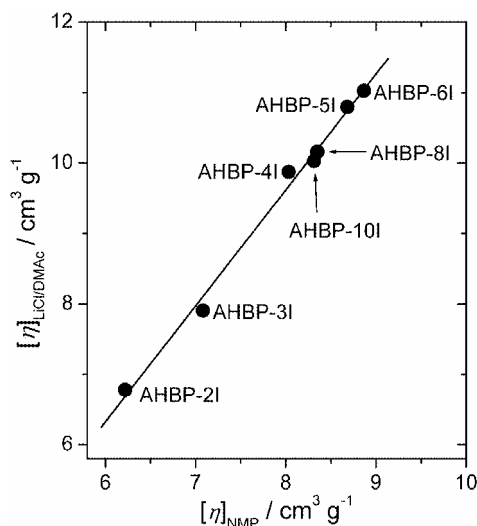


Fig. 2. Correlation of the limiting viscosity numbers determined for AHBP of the series I in LiCl/DMAc and in NMP.

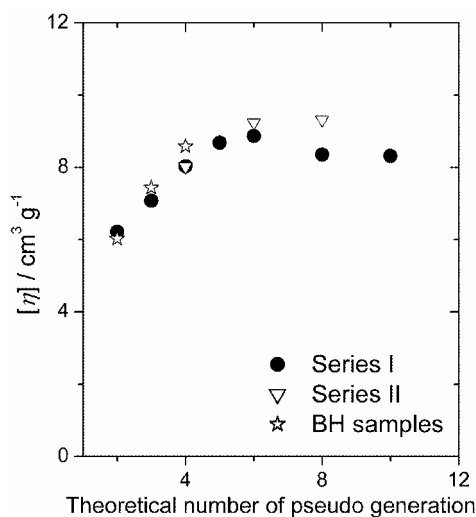


Fig. 3. Dependence of $[\eta]$ for the AHBPs determined in NMP vs. the theoretical number of pseudo generations.

The dependences of $\log [\eta]$ vs. $\log M_w$ for AHBPs of series I from the second up to the sixth pseudo generation in LiCl/DMAc and NMP are presented in Fig. 4. The values of the weight average molar mass of the AHBPs were calculated from

the values of the polydispersity index, $Q = (M_w/M_n)_{\text{GPC}}$, determined by the GPC technique (Table V) and the corresponding values of the number average molar mass, $(M_n)_{\text{VPO}}$, determined from VPO measurements (Table I). Using the Kuhn–Mark–Houwink–Sakurada (KMHS) equation ($[\eta] = K_\eta M^a$) and the dependences presented in Fig. 4, the values of the exponent a and constant K_η for the investigated AHBP in NMP and LiCl/DMAc were determined and given in Table III, in which are also given the corresponding values for the same samples in DMAc.

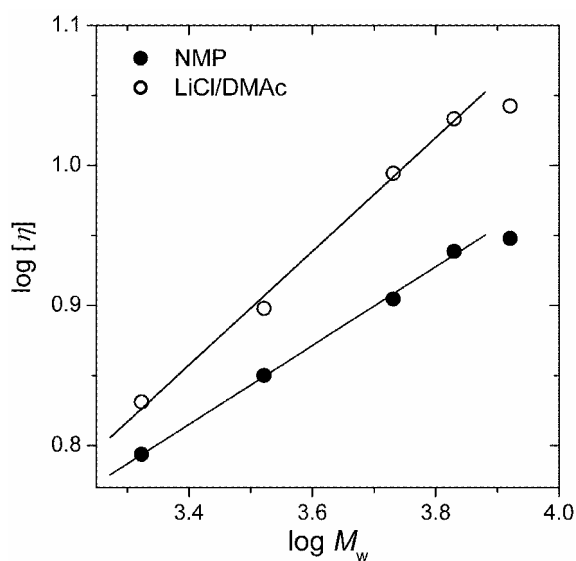


Fig. 4. Dependence of $\log [\eta]$ vs. $\log M_w$ for the AHBPs of series I, obtained using the values of $[\eta]$ determined in NMP and LiCl/DMAc as solvents.

TABLE III. Values of the exponent a and constant K_η determined from the KMHS equation in different solvents at 25 °C for the investigated AHBPs

Sample group	LiCl/DMAc		NMP		DMAc	
	a	K_η	a	K_η	a	K_η
Series I	0.40	0.30	0.28	0.72	0.25	1.44

The results presented in Fig. 4 clearly show that there is a good linear relationship between $\log [\eta]$ and $\log M_w$ up to the fifth pseudo generation and that for this region of molar masses, the parameters K_η and a can be used for the determination of molar mass by viscosimetry for samples synthesized in the same manner as the AHBP of series I. It has been already stated elsewhere that for branched polymers, a linear $\log [\eta]$ – $\log M$ relationship is only obtained for very narrow molar mass ranges.²⁰ The exponent a from the KMHS equation is also a measure of the solvent quality for some linear polymers. In good solvents, the value of a is usually between 0.60 and 0.85, while $a \leq 0.50$ is typical only for poor solvents.²⁰ The obtained values of the exponent a (Table III) are all lower than 0.50, which is a characteristic only for highly branched polymers in good solvents. The values of the exponent a increases with solvent quality. However,

the division of the solvents for hyperbranched polymers into good and poor according to the a values is not yet possible.

Hydrodynamic radius of macromolecules in solution, R_η , is connected with $[\eta]$ and the molar mass, M , through the Einstein equation:

$$R_\eta = (0.3[\eta]M\pi^{-1}N_A^{-1})^{1/3} \quad (3)$$

where N_A is Avogadro's number. By introducing the determined values of $[\eta]$ (Table II) and molar mass (M_w)_{real}, (Table V) into Eq. (3), the values of R_η for the investigated AHBPs in four different solvents were calculated and given in Table IV. From the results given in Table IV, it can be seen that the value of R_η of AHBPs depends on the solvent quality in the same manner as for linear polymers. However, due to the specific molecular structure of AHBPs this dependence is not as strong as for linear polymers. As was expected, the largest dimensions of these hyperbranched polyesters were obtained in LiCl/DMAc. The small values of R_η of AHBPs in solution, the large number of functional groups and, simultaneously, the low viscosity of their solutions provide the successful application of AHBPs for the production of special coatings, ink for the printers or drug carriers.²¹

TABLE IV. Values of the hydrodynamic radius, R_η , for the investigated AHBPs in LiCl/DMAc, NMP, DMAc and THF/CH₃OH at 25 °C

Sample	$(R_\eta)_{\text{LiCl/DMAc}} / \text{nm}$	$(R_\eta)_{\text{NMP}} / \text{nm}$	$(R_\eta)_{\text{DMAc}} / \text{nm}$	$(R_\eta)_{\text{THF/CH}_3\text{OH}} / \text{nm}$
AHBP-2I	1.3	1.3	1.3	/
AHBP-3I	1.6	1.5	1.5	/
AHBP-4I	2.0	1.9	1.8	1.8
AHBP-5I	2.3	2.2	2.0	1.9
AHBP-6I	2.4	2.3	2.2	2.0
AHBP-8I	2.3	2.2	2.2	2.0
AHBP-10I	2.2	2.0	2.0	1.9
AHBP-4II	–	2.4	–	–
AHBP-8II	–	2.2	–	–
BH-2	1.3	1.2	1.2	–
BH-3	2.1	1.9	–	1.7
BH-4	2.3	2.2	–	2.0

GPC Measurements

The determination of the molar mass distribution of the investigated AHBPs and three fractions of the sample AHBP-6I was performed by the GPC technique in the manner described in the Experimental. Linear polystyrene standards were employed for the calibration of the instrument, since adequate AHBP standards are not available. As branched macromolecules have a much lower hydrodynamic radius than the corresponding linear macromolecules of the same molar mass,

the obtained values of M_w and M_n can not be consider as correct. Therefore, the GPC chromatograms of the investigated AHBPs were used only for a comparison of the shape of their traces and to calculate the values of the polydispersity index, Q , as well as for the calculation of $(M_w)_{\text{real}}$.

As illustrations, the GPC chromatograms of the AHBPs of series I and the commercial samples are presented in Fig. 5a and 5b, respectively. From the obtained GPC results for all investigated AHBP, as well as for the three fractions of the sample AHBP-6I, the values of the molar masses $(M_w)_{\text{GPC}}$ and $(M_n)_{\text{GPC}}$ and the polydispersity index Q were calculated and are given in Table V.

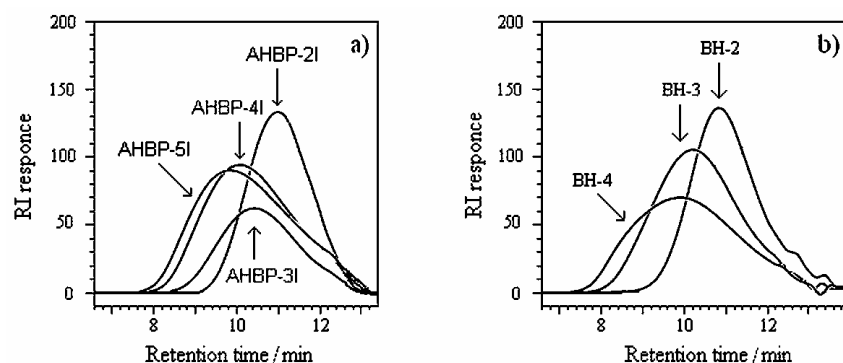


Fig. 5. GPC chromatograms of AHBPs a) synthesized by the pseudo-one-step procedure (samples of series I) and b) commercial AHBPs.

TABLE V. Values of the molar masses $(M_w)_{\text{GPC}}$ and $(M_n)_{\text{GPC}}$, polydispersity index, Q , $(M_w)_{\text{real}}$ and limiting viscosity number of the fractions determined in NMP, $[\eta]_{\text{F}}$, of the investigated hyper-branched polyesters and selected fractions

Sample	$(M_w)_{\text{GPC}} / \text{g mol}^{-1}$	$(M_n)_{\text{GPC}} / \text{g mol}^{-1}$	Q	$(M_w)_{\text{real}} / \text{g mol}^{-1}$	$[\eta]_{\text{F}} / \text{cm}^3 \text{g}^{-1}$
AHBP-2I	1041	749	1.39	—	—
AHBP-3I	1655	1008	1.64	3324	—
AHBP-4I	2238	1172	1.91	5384	—
AHBP-5I	2688	1213	2.22	6758	—
AHBP-6I	2993	1287	2.33	8330	—
F1	5581	2260	2.47	—	10.4
F2	3832	1973	1.94	—	8.7
F3	1080	771	1.40	—	6.5
AHBP-8I	2994	1348	2.22	7928	—
AHBP-10I	2111	1155	1.83	6500	—
AHBP-4II	2475	1189	2.08	11263	—
AHBP-6II	2912	1179	2.47	—	—
AHBP-8II	2674	1148	2.33	7652	—
BH-2	1120	782	1.43	1920	—
BH-3	2227	1147	1.94	5977	—
BH-4	3454	1242	2.78	7550	—

The results presented in Fig. 5 and Table V show that the GPC traces, *i.e.*, the molar mass distributions of the AHBPs, become broader with increasing theoretical number of generations, *i.e.*, up to the sixth pseudo generation. Only for the sample AHBP-2I was a symmetrical GPC profile obtained, while for the samples of higher generation number, a broad tail on the low molar mass side of the distribution can be observed. This specific shape of the GPC traces is a consequence of side reactions responsible for the formation of small molar mass AHBP molecules, the portion of which increases with increasing pseudo generation, during the main polycondensation reaction.^{1h} The GPC chromatograms of the AHBPs synthesized by the one-step procedure have a similar profile as those synthesized by the pseudo-one-step procedure, but they also have slightly higher values of Q . This is in good agreement with the results presented by Hult *et al.*, who showed that the slow monomer addition method (pseudo-one-step procedure for the synthesis) could reduce the polydispersity of hyperbranched polyesters.^{1a}

As it was expected, the molar mass averages determined by GPC using linear polystyrene standards for calibration are lower than the theoretical values and results obtained by VPO (Table I). The number average molar masses obtained by GPC and VPO measurements for the AHBP of series I are plotted in Fig. 6. It can be observed that a relatively good linear correlation between $(M_n)_{\text{GPC}}$ and $(M_n)_{\text{VPO}}$ for the samples from the third up to the eighth pseudo generation was obtained, which indicates that the ratio $(M_n)_{\text{GPC}}/(M_n)_{\text{VPO}}$ does not change with increasing molar mass. Assuming that determined values of Q are real, the values of the real weight average molar mass of the examined AHBPs, $(M_w)_{\text{real}}$, were calculated using the equation:

$$(M_w)_{\text{real}} = Q (M_n)_{\text{VPO}} \quad (4)$$

The co-calculated values of $(M_w)_{\text{real}}$ are also given in Table V. These values were used for the determination of the calibration diagram $\log [\eta] - \log M$ and for the calculation of the “shrinking” factor, g' , of the branched AHBP macromolecules.

Most of the self-synthesized samples were fractionated using the precipitation fractionation method to obtain three fractions in order to investigate in which manner the degree of branching changes with molar mass within one sample. According to the obtained values of the limiting viscosity number, $[\eta]_{\text{F}}$, (Table V), it was concluded that fractionation was successful. However, when the GPC method was used to re-fractionate the AHBP fractions, different results were obtained. As an illustration, the GPC traces of AHBP-6I and three fractions obtained by precipitation fractionation method are presented in Fig. 7. The corresponding values of $(M_w)_{\text{GPC}}$, $(M_n)_{\text{GPC}}$ and Q are given in Table V. From these results it can be observed that polydispersity increased from the third up to the first fraction, *i.e.*, that the molar mass distribution becomes broader with increasing degree of polymerization. However, the fact that value of Q for the first fraction is higher than for the parent sample indicates that fractionation under described experi-

mental conditions was not efficient. Therefore, the values of the degree of branching for the fractions of an AHBP cannot be accepted as correct and, consequently, they are not presented in this work.

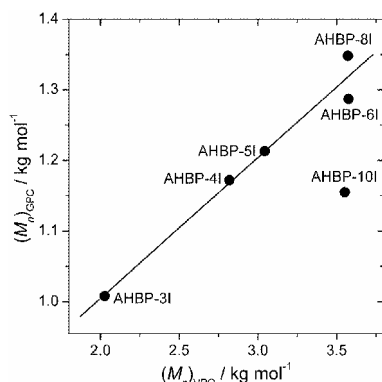


Fig. 6. Correlation of the number average molar mass obtained from GPC and VPO measurements for the AHBPs of series I.

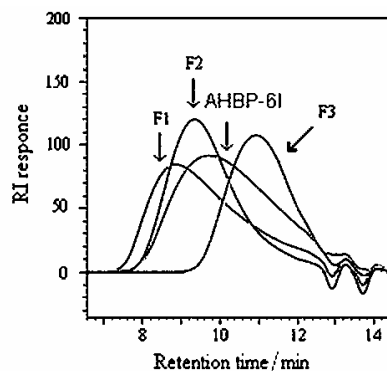


Fig. 7. GPC chromatograms of AHBP-6I and three fractions obtained by the precipitation fractionation method.

Using the results obtained by the GPC technique, the values of the “shrinking” factor, g' , of the macromolecular coils of the examined AHBPs in relation to linear polymers of corresponding molar masses were calculated:

$$g' = [\eta]_{\text{HBP}} / [\eta]_{\text{L}} \quad (5)$$

where $[\eta]_{\text{HBP}}$ and $[\eta]_{\text{L}}$ represent the limiting viscosity numbers of the given hyperbranched polymer and its linear analogue, respectively. The calculation of shrinking factor was performed using the fact that the product of the limiting viscosity number and molar mass at a certain elution volume is always the same and independent of the polymer type.²² Therefore, it can be written:

$$[\eta]_{\text{HBP}} M_{\text{HBP}} = [\eta]_{\text{L}} M_{\text{L}} \quad (6)$$

where M_{HBP} and M_{L} are the molar masses of the hyperbranched polyesters and the linear polymers (polystyrene) used for the calibration, respectively. From the Eq. (6), it follows that g' can be calculated as $M_{\text{L}} / M_{\text{HBP}}$. The values of M_{L} were calculated by determination of the retention time which corresponds to the position of the peak in the GPC traces of different AHBPs. Then these retention times were used to determine the molar masses of the corresponding polystyrene from the calibration curve. On the other hand, for M_{HBP} , the weight average molar mass $(M_w)_{\text{real}}$ was used (Table V). The determined values of g' for the AHBPs are listed in Table VI. As can be seen, the values of g' for all the AHBPs are between 0.27 and 0.57. Similar results were obtained for other hyperbranched polymers.²³

TABLE VI. Values of the “shrinking” factor, g' , for the investigated AHBPs

Sample	g'	Sample	g'
AHBP-2I	0.44	AHBP-10I	0.27
AHBP-3I	0.45	AHBP-8II	0.30
AHBP-4I	0.35	BH-2	0.57
AHBP-5I	0.34	BH-3	0.29
AHBP-6I	0.31	BH-4	0.31
AHBP-8I	0.32		

CONCLUSIONS

The results obtained in this study show that of the tested ones, the best solvent for the examined AHBPs is 0.7 mass % solution of LiCl in DMAc. In *N*-methyl-2-pyrrolidone, the values of $[\eta]$ increase up to the sixth pseudo generation. The slight decrease of $[\eta]$ for samples of a higher pseudo generation is the consequence of the occurrence of side reactions during the synthesis of investigated AHBPs, which hindered a further increase of the molar mass. The values of $[\eta]$ for the AHBPs synthesized by the one-step procedure were slightly higher than those of the corresponding samples synthesized by the pseudo-one-step procedure, indicating a slight influence of the synthesis procedure on the behaviour of AHBPs in dilute solutions. The calculated values of the exponent a from the KMHS equation for the samples of series I in different solvents are lower than 0.50, because of the highly branched structure of these polymers. The values of the “shrinking” factor of the examined AHBPs are similar to those presented in the literature for other hyperbranched polymers.

ИЗВОД

СВОЈСТВА АЛИФАТСКИХ ХИПЕРРАЗГРАНАТИХ ПОЛИЕСТАРА
У РАЗБЛАЖЕНИМ РАСТВОРИМАЈАСНА ВУКОВИЋ¹, MANFRED D. LECHNER¹ и СЛОБОДАН ЈОВАНОВИЋ²¹*Institute for Chemistry, University of Osnabrueck, Barbarastraße 7, 49069 Osnabrueck, Germany* и
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У овом раду су приказани резултати добијени испитивањем утицаја процедуре за синтезу, броја псеудогенерације и степена гранања хидрокси-функционалних алифатских хиперразгранатих полиестара (AHBP) на вредност граничног вискозитетног броја, $[\eta]$, хидродинамичког радијуса, R_h , моларне масе и индекса полидисперзности, Q . Испитане су две серије AHBP, синтетисане од 2,2-бис(хидроксиметил)пропионске киселине и ди-триметил-олпропана коришћењем “pseudo-one-step” и “one-step” процедуре. Добијени резултати показују да су вредности $[\eta]$ и R_h за све испитане узорке највеће у 0.7 % раствору LiCl у *N,N*-диметилацетамиду (LiCl/DMAc), што указује да је од коришћених овај растварач најбољи. Вредности $[\eta]$ у *N*-метил-2-пиролидону (NMP) расту до шесте псеудогенерације, након чега долази до благог опадања као последица присуства производа споредних реакција насталих у току синтезе. Појава производа споредних реакција је такође потврђена на основу карактеристичног облика GPC хроматограма. За узорке AHBP синтетисане “pseudo-one-step” процедуром добијена је добра линеарна зависност између $\log [\eta]$ и $\log M_w$ до пете псеудогенера-

ције, када су као rastvarачи коришћени LiCl/DMAc, NMP и DMAc. Вредности степена контракције макромолекулског клупка, g' , су израчунате за све испитане узорке АНБР.

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REFERENCES

1. a) E. Malmström, M. Johansson, A. Hult, *Macromolecules* **28** (1995) 1698; b) M. L. Mansfield, L. I. Klushin, *J. Phys. Chem.* **96** (1992) 3994; c) L. J. Hobson, W. J. Feast, *Polymer* **40** (1999) 1279; d) M. Sun, Z. Bo, *J. Polym. Sci. A* **45** (2007) 111; e) M. Malkoch, H. Claesson, P. Löwenhielm, E. Malmström, A. Hult, *J. Polym. Sci. A* **42** (2004) 1758; f) V. Petkov, V. Parvanov, D. Tomalia, D. Swanson, D. Bergstrom, T. Vogt, *Solid State Commun.* **134** (2005) 671; g) D. Parker, W. J. Feast, *Macromolecules* **34** (2001) 2048; h) J. Vuković, M. D. Lechner, S. Jovanović, V. Vodnik, Unpublished results
2. a) M. Johansson, A. Hult, *J. Coat. Technol.* **67** (1995) 35; b) Y. Zhang, L. Wang, T. Wada, H. Sasabe, *Macromol. Chem. Phys.* **197** (1996) 667; c) T. Griebel, G. Maier, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **41** (2000) 89; d) M. Johansson, E. Malmström, A. Hult, *J. Polym. Sci. A* **31** (1993) 619; e) Y. H. Kim, O. W. Webster, *Macromolecules* **25** (1992) 5561; f) R. Esfand, D. A. Tomalia, *Drug Discovery Today* **6** (2001) 427; g) K. Urich, *Trends in Polym. Sci.* **5** (1997) 388; h) C.-Y. Hong, Y.-Z. You, D. Wu, Y. Liu, C.-Y. Pan, *Macromolecules* **38** (2005) 2606; i) E. Malmström, M. Johansson, A. Hult, *Macromol. Chem. Phys.* **197** (1996) 3199
3. D. A. Tomalia, A. M. Naylor, W. A. Goddard, *Angew. Chem. Int. Ed. Engl.* **29** (1990) 138
4. I. B. Rietveld, J. A. M. Smit, *Macromolecules* **32** (1999) 4608
5. T. H. Mourey, S. R. Turner, M. Rubinstein, J. M. J. Fréchet, C. J. Hawker, K. L. Wooley, *Macromolecules* **25** (1992) 2401
6. R. L. Lescanec, M. Muthukumar, *Macromolecules* **23** (1990) 2280
7. J. M. J. Fréchet, C. J. Hawker, I. Gitsov, J. W. Leon, *J. Macromol. Sci. Pure Appl. Chem.* **A33** (1996) 1399
8. L. J. Hobson, W. J. Feast, *Chem. Commun.* **21** (1997) 2067
9. A. H. Widmann, G. R. Davies, *J. Comput. Theor. Polym. Sci.* **8** (1998) 191
10. J. Aerts, *J. Comput. Theor. Polym. Sci.* **8** (1998) 49
11. S. R. Turner, B. I. Voit, T. H. Mourey, *Macromolecules* **26** (1993) 4617
12. J. Vuković, M. D. Lechner, S. Jovanović, *Macromol. Chem. Phys.* **208** (2007) 2321
13. C. J. Hawker, R. Lee, J. M. J. Fréchet, *J. Am. Chem. Soc.* **113** (1991) 4583
14. M. L. Huggins, *J. Am. Chem. Soc.* **64** (1942) 2716
15. D. Braun, H. Cherdron, W. Kern, *Praktikum der makromolekularen organischen Chemie* 3. Auflage, Hüthig, Heidelberg, (1979)
16. A. Luciani, C. J. G. Plummer, T. Nguyen, L. Garamszegi, J.-A. E. Månson, *J. Polym. Sci. B* **42** (2004) 1218
17. E. Žagar, M. Žigon, *J. Chromatogr. A* **1034** (2004) 77
18. J. Vuković, *M.Sc. Thesis*, Faculty of Technology and Metallurgy, University of Belgrade (2003) p. 53
19. E. Žagar, M. Žigon, *Macromolecules* **35** (2002) 9913
20. W.-M. Kulicke, C. Clasen, *Viscosimetry of Polymers and Polyelectrolytes*, Springer-Verlag, Berlin, Heidelberg, New York, 2004, p. 83
21. M. E. Mackay, G. Carmezini, *Chem. Mater.* **14** (2002) 819
22. E. Schröder, G. Müller, K.-F. Arndt, *Polymer characterization*, Hanser Publishers, Munich, Vienna, New York (1988)
23. K. Ishizu, D. Takahashi, H. Takeda, *Polymer* **41** (2000) 6081.