

Ionization of Acid-Functionalized Hyperbranched Polyesters

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Abstract: Ionization of second- and third-generation hyperbranched polyesters functionalized by different acids was studied by mathematic simulation of experimental titration curves using the CPESPP programme. It was found that polyesters functionalized with carboxyethyl groups are ionized blockwise, while those functionalized with acrylic groups are ionized stepwise. Moreover, such polyesters show different self-association ability which decreases when going to greater generations.

Key words: Functionalized hyperbranched polyesters • Polyacids • Simulation • Ionization

INTRODUCTION

Preparation of systems from nanosized particles with well-defined sizes and shapes is of great today's interest having in mind their application for different scientific and practical purposes, for example, in polymer material science, electronics and microelectronics, optics, biology, medicine and ecology. The attention has been paid in recent decade to nanostructured polymers composed of macromolecules with complex architecture, such as dendrimers and hyperbranched polymers (HBPs) [1, 2]. Of particular interest are HBPs being produced commercially [3] as well as the methods for their modification depending on a specific application problem.

Physical-chemical properties of dendrimers and HBPs sharply contrast sometimes with those of linear polymers [4]. Acid-base properties of weak linear polyelectrolytes have been studied thoroughly [5-7]. Protonation of a linear polyelectrolyte having the only type of ionized groups proceeds via two stages, with a plateau occurring half-way of protonation. This plateau refers to a stable transition state when protonated and unprotonated groups alternate along a chain, which corresponds to the least electrostatic repulsion between adjacent groups.

These phenomena were studied quantitatively by using the Ising model [6]. Polyfumaric acid and polymaleic acid were used. Interaction of the proton with ionizable groups was divided into short-range (ΔpK_{short}) and long-range (ΔpK_{long}) order interactions calculated by:

$$\Delta pK_{\text{short}} = \lg a + \lg[(1-a)/a] \quad (1)$$

where $a = a/a_0$ (a is the activity of dissociated groups, a_0 is the activity of undissociated groups), $[\alpha]$ is the dissociation rate which can be found from general distribution function:

$$\Delta pK_{\text{long}} = 0.4343\alpha/kT \sum_{P_1=P_s+1}^{2N} (e^2/DR_{P_1}) \exp(-\kappa R_{P_1}) \quad (2)$$

where κ is the Debye-Hückel parameter; D is the dielectric permittivity, R_p is the distance between groups; summation is performed over the pairs not included in the equation (1). Authors took into consideration the following: the distance between groups in the case of short-range order interaction, carboxylic group configuration, the dielectric constant around the ionized groups and hydrogen bonding between adjacent groups.

Simulation of the ionization of polyfumaric and polymaleic acids allowed making a conclusion about the effect of configuration on the dissociation of polyacids, so the applicability of simulation, including the Ising model, was verified. At the same time, this simulation showed drawbacks, such as the impossibility to describe asymmetric curve patterns due to the symmetry of the model itself as well as complicated calculation of long-range order interactions.

It is worthwhile noting that the papers devoted to ionization of branched polymers functionalized with acidic groups are lacking. The ionization of branched polymers, including dendrimers and HBPs, has been studied as applied mostly to bases [8, 9].

This work proposes the method for studying the ionization of HBPs with terminal acidic groups by mathematic simulation of experimental titration curves using the CPESP (Complex formation Parameters of Equilibria in Solution with Solid Phases) programme [10]. This programme gives reproducible and adequate results from the calculation of equilibrium parameters in systems of various complexities, including calculation of ionization parameters of polyacids as well as heteronuclear and heteroligand complex compounds.

Experimental

Reagents: A second-generation hyperbranched Boltorn H20 polyesterpolyol (16 hydroxyl groups, $M_r = 1747$ g/mole, the hydroxyl value = 515 mg/g KOH, $T_m = 80-110^\circ\text{C}$) and a third-generation hyperbranched Boltorn H30 polyesterpolyol (32 hydroxyl groups, $M_r = 3560$ g/mole, the hydroxyl value = 480-520 mg/g KOH), both based on ethoxylated pentaerythritol as a nucleus and 2,2-bis(methylol)propionic acid as a monomer (Perstorp Speciality Chemicals AB, Sweden); succinic anhydride and maleic anhydride (Alfa Aesar); NaClO_4 salts; diethyl ether; 1,4-dioxane; and acetone (Acros) were used.

Synthesis of Polyester Polycarboxylic Acids I-III [11]: A sample (0.003 mole) of Boltorn H20 or Boltorn H30 was heated up to 140°C , cooled down to 50°C and dissolved in 1,4-dioxane (15 ml). A mixture contained the heated solution of Boltorn H20 or Boltorn H30, a stoichiometric amount of succinic anhydride or maleic anhydride (0.014 or 0.046 mole, at mole ratio of 1:16 or 1:32, added to Boltorn H20 or Boltorn H30 solution correspondingly) and SnCl_2 (1 wt.% of the initial polyesterpolyol amount) was prepared. The mixture was stirred at 100°C for 36 hours,

cooled down and treated with diethyl ether or benzene in the case of reaction with succinic anhydride or maleic anhydride correspondingly. The resulting products were separated and dried under vacuum. Both composition and structure of hyperbranched polyester polyacids **I-III** were determined by means of IR-spectroscopy and ^1H , ^{13}C NMR in solution and in solid and represented in article [11]. The functionalization degree was determined by means of potentiometric titration and gel permeation chromatography.

The initial and working solutions of polyester polycarboxylates were prepared by dissolving accurately weighed samples in organic solvents and used within 24 hours. Titration of reagents was carried out with NaOH solution prepared by using accurately weighed sample in water-acetone solution and filtered from carbonates. The solutions prepared were diluted with the corresponding solvents to achieve a fixed concentration.

Instrumentation: The pH-value was measured at $25 \pm 0.05^\circ\text{C}$ with an accuracy of 0.01 logarithmic pH units with InoLab pH7310 set4 pH-meter. A glass electrode previously soaked in mixed solvent (a 50% water-aceton mixture) for 24 hours and calibrated with buffer solutions prepared in the same solvent was used as the indicating electrode. For determining the pH-value of water-organic solutions with glass electrode the correction factor $\lg \Delta_H$ was calculated by:

$$\lg \Delta_H = pH_{calc.} - pH_{exp.} \quad (3)$$

where $pH_{calc.}$ is the calculated pH-value; $pH_{exp.}$ is experimental pH-value.

Simulation of Ionization Equilibria: Acid dissociation constants and base protonation constants were determined by pH-metric titration. Experimental data for calculating stepwise pK -values and the maximum content of ionized forms accumulated were processed by using mathematic simulation with the CPESP programme to create a model describing all theoretically possible forms existing in solution. The CPESP programme relies on the Brinkley method. According to this method a stoichiometric matrix \hat{A} where the lines are the vectors of stoichiometric coefficients of reactions is obtained for the system chemical composition of which is given by s different molecules joined together by r chemical reactions. These independent chemical reactions give the basis of composition variation which is complemented by

the space of vectors expressed in $m=s-r$, where r is the amount of independent reactions with stoichiometric coefficients $[ny]_{ij}$ expressed in canonical form:

$$\sum_{j=1}^m v_{ij} b_j = A_i \quad (4)$$

Here, b_j is the series of substances referred to as independent components (basis particles), but products A_i are all reacting substances related to m vectors of the basis which complements a subspace. For calculating equilibrium composition of solution the Brinkley method uses linear mass balance relations; with the equilibrium condition in the form of the law of mass action being solved in terms of concentrations of particles not included in the basis:

$$a_i = \exp(\ln \beta_i + \sum_j v_{ij} \ln b_j)$$

$$b_j^0 = \sum_{i=1}^s v_{ij} \exp(\ln \beta_i + \sum_j v_{ij} \ln b_j)$$

where $[\beta]_i$ is the concentration constant of the law of mass action, b_j is the concentration of basis particles, b_j^0 is a total concentration of the component j in solution, a_i are concentrations of complex forms generated by reactions (4) and formal reactions of creating the particle b_j from itself.

For two-basis and multi-basis systems the additional functions are used, such as the component binding function

$$a_{ij} = \frac{v_{ij} a_i}{b_j^0} \quad (5)$$

An average value of the component b_1 in terms of b_2 denotes the average amount of the component b_1 bound in complexes per a mole of the component b_2 :

$$n_{l,j} = n_{12} = \frac{b_1^0 - b_1}{b_2^0}$$

By using the mass balance equation for b_1^0 and b_2^0 as well as definitions of the $[\alpha]_{ij}$ -values (5) the following equation can be obtained:

$$\sum_{i=2}^s v_{i1} a_{i2} = n_{12},$$

which can be expanded with the expression:

$$\bar{n}_{12} = \frac{\sum_{i=2}^s v_{i1} \beta_i b_1^{v_{ij}}}{\sum_{i=2}^s \beta_i b_1^{v_{ij}}} \quad (6)$$

The relationship between \bar{n}_{12} and b_1 according to the equation (6) is usually referred to as the formation function. Semilogarithmic plotting of this relationship is the formation curve.

The CPESP programme is applied for solving direct problems (determination of equilibrium composition of a system) and inverse problems (finding a model of the object under study and determination of parameters characteristic of this model). Assessment of the reliability of solution is performed using the Fisher criterion (F):

$$F = \sum_{i=1}^N (\bar{n}_{exp,i} - \bar{n}_{calc,i})^2 \frac{1}{\sigma^2 \bar{n}_{calc,i}^2} \quad (7)$$

where $\bar{n}_{exp,i}$ and $\bar{n}_{calc,i}$ are experimentally measured and calculated formation function values correspondingly; i and N are the experiment number and the number of experiments; $[\sigma]$ is the relative measurement error $\frac{\sigma}{\bar{n}}$.

The maximum correlation between experimental and theoretically calculated data ($R < 3\%$) allows determining the parameters of significant equilibria.

RESULTS AND DISCUSSION

Boltorn H grade polyesterpolyols [3], namely Boltorn H20 and Boltorn H30 were used as a basis for the synthesis of polyester polycarboxylic acids **I-III** [11, 12] (Fig. 1). Hyperbranched polyesterpolyols functionalized with different acidic and basic groups are the advanced biologically active compounds which can be used as pharmaceutical drugs as well as carriers for pharmaceuticals and genetic material. For an efficient application of such polyesterpolyols in the fields mentioned, one needs to have an idea of how these structures are ionized. It should be noted that using the analysis of plotted titration curves is impossible for

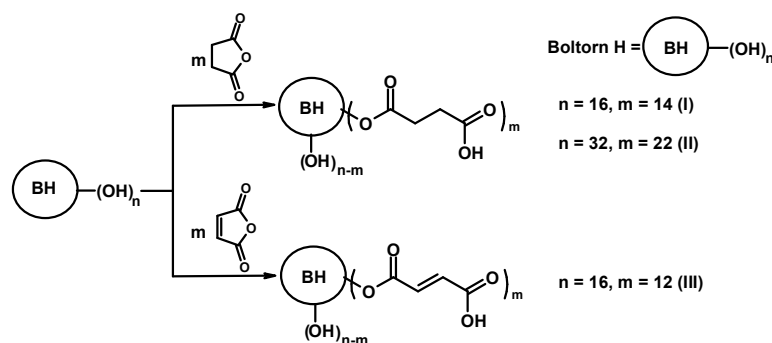


Fig. 1: Scheme of synthesis the compounds I, II, III.

Table 1: Parameters of ionization equilibria in solution of compound I ($V_1=5$ ml, $C_T=8.7 \times 10^{-3}$ M, $C_{NaOH}=0.089$ M) $F_{\text{min}}=1.425$; $F_{\text{max}}=2.29 \times 10^{-2}$; $R=7.403 \times 10^{-3}$.

#	Equilibria	pK_{gen}	Equilibria	pK_{step}	Share, %
1	$H_{14}L$		$H_{14}L$		40.13
2	$H_{14}L \rightleftharpoons H_{13}L^- + H^+$	4.42±0.14	$H_{14}L \rightleftharpoons H_{13}L^- + H^+$	4.42	20.49
4	$H_{14}L \rightleftharpoons H_{11}L^{3-} + 3H^+$	13.81±0.28	$H_{12}L^{2-} \rightleftharpoons H_{11}L^{3-} + H^+$	4.21	47.61
5	$H_{14}L \rightleftharpoons H_{10}L^{4-} + 4H^+$	19.34±0.96	$H_{11}L^{3-} \rightleftharpoons H_{10}L^{4-} + H^+$	5.53	25.28
6	$H_{14}L \rightleftharpoons H_9L^{5-} + 5H^+$	25.03±2.38	$H_{10}L^{4-} \rightleftharpoons H_9L^{5-} + H^+$	5.69	15.10
7	$H_{14}L \rightleftharpoons H_8L^{6-} + 6H^+$	30.25±1.00	$H_9L^{5-} \rightleftharpoons H_8L^{6-} + H^+$	5.22	40.04
9	$H_{14}L \rightleftharpoons H_6L^{8-} + 8H^+$	42.05±0.38	$H_7L^{7-} \rightleftharpoons H_6L^{8-} + H^+$	5.4	46.34
11	$H_{14}L \rightleftharpoons H_4L^{10-} + 10H^+$	54.60±0.20	$H_5L^{9-} \rightleftharpoons H_4L^{10-} + H^+$	2.46	56.59
13	$H_{14}L \rightleftharpoons H_2L^{12-} + 12H^+$	68.18±0.15	$H_3L^{11-} \rightleftharpoons H_2L^{12-} + H^+$	6.06	71.53
14	$H_{14}L \rightleftharpoons HL^{13-} + 13H^+$	76.10±0.21	$H_2L^{12-} \rightleftharpoons HL^{13-} + H^+$	7.92	99.9
16	$2H_{14}L \rightleftharpoons (H_{14}L)_2$	2.30±0.31			12.04
17	$2H_{14}L \rightleftharpoons (H_{14}L)_2$	10.69±0.04			36.9
18	$4H_{14}L \rightleftharpoons (H_{14}L)_4$	1.22±0.263			29.17

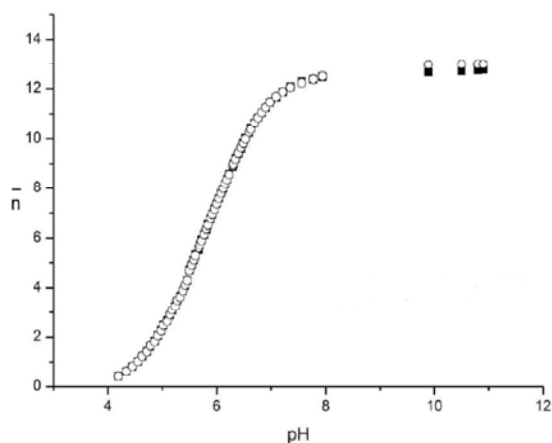


Fig. 2: Experimental (■) and calculated (○) dependencies of the Bjerrum function \bar{n} on the pH-value for the compound I.

studying similar macro objects since ionization stages are not pronounced but ionization constants are defined by the number of corresponding micro constants. Therefore, the mechanism of ionization of functionalized hyperbranched

polyesterpolyols has been studied by mathematic simulation of ionization equilibria using the CPESPP programme.

Consider the ionization of hyperbranched polyester containing 14 propanoic acid fragments (compound I). Both experimental and theoretically calculated dependencies of the Bjerrum function on the pH-value show the only stage (Fig. 2).

The maximum Bjerrum function value is 13. Basing on the number of functional (carboxylic) groups, a stoichiometric matrix comprised 14 equilibria for the ionization of 14 carboxylic groups was obtained. Characterization of the experimental curve proved to be satisfactory, except for the initial part of the curve. Since carboxylic acids are characterized by self-association which can affect titration curve profile in the region of lower pH-values, the equilibria of formation of dimers, trimers, tetramers and their ionized forms were introduced into the model. In this case, the correlation coefficient was 0.74%, several ionized forms of dimers and tetramers accumulated were detected. The most significant equilibria, forms and parameters of ionization pK_{general} , pK_{stepped} , accumulation share of ionized form are presented in Table 1.

Table 2: Parameters of ionization equilibria in solution of compound **II** ($V_{II}=5$ ml, $C_{II}= 4.82 \times 10^{-3}$ M $C_{NaOH}= 0.0796$ M) $F_{min}=2.503$; $F_{pr}=5.96 \times 10^{-2}$; $R=1.048 \times 10^{-2}$.

#	Equilibria	pK_{gen}	Equilibria	pK_{step}	Share, %
1	$H_{22}L$		$H_{22}L$		21.36
2	$H_{22}L \rightleftharpoons H_{21}L^- + H^+$	4.60±0.18	$H_{22}L \rightleftharpoons H_{21}L^- + H^+$	4.60	35.87
3	$H_{22}L \rightleftharpoons H_{20}L^{2-} + 2H^+$	~10.06	$H_{21}L^- \rightleftharpoons H_{20}L^{2-} + H^+$	5.46	21.64
4	$H_{22}L \rightleftharpoons H_{19}L^{3-} + 3H^+$	15.25±0.63	$H_{20}L^{2-} \rightleftharpoons H_{19}L^{3-} + H^+$	5.19	37.93
6	$H_{22}L \rightleftharpoons H_{17}L^{5-} + 5H^+$	26.50±4.11	$H_{18}L^{4-} \rightleftharpoons H_{17}L^{5-} + H^+$	1.89	51.47
8	$H_{22}L \rightleftharpoons H_{15}L^{7-} + 7H^+$	38.76±6.72	$H_{16}L^{6-} \rightleftharpoons H_{15}L^{7-} + H^+$	5.24	33.37
9	$H_{22}L \rightleftharpoons H_{14}L^{8-} + 8H^+$	45.08±1.73	$H_{15}L^{7-} \rightleftharpoons H_{14}L^{8-} + H^+$	6.32	29.92
11	$H_{22}L \rightleftharpoons H_{12}L^{10-} + 10H^+$	57.87±2.91	$H_{13}L^{9-} \rightleftharpoons H_{12}L^{10-} + H^+$	2.87	45.51
12	$H_{22}L \rightleftharpoons H_{11}L^{11-} + 11H^+$	64.95±1.81	$H_{12}L^{10-} \rightleftharpoons H_{11}L^{11-} + H^+$	7.08	19.44
14	$H_{22}L \rightleftharpoons H_9L^{13-} + 13H^+$	78.3±2.21	$H_{10}L^{12-} \rightleftharpoons H_9L^{13-} + H^+$	2.93	58.84
16	$H_{22}L \rightleftharpoons H_7L^{15-} + 15H^+$	93.32±2.10	$H_8L^{14-} \rightleftharpoons H_7L^{15-} + H^+$	4.00	14.78
17	$H_{22}L \rightleftharpoons H_6L^{16-} + 16H^+$	100.2±2.1	$H_7L^{15-} \rightleftharpoons H_6L^{16-} + H^+$	6.88	57.47
19	$H_{22}L \rightleftharpoons H_4L^{18-} + 18H^+$	115.7±2.1	$H_5L^{17-} \rightleftharpoons H_4L^{18-} + H^+$	3.70	94.13
20	$H_{22}L \rightleftharpoons H_3L^{19-} + 19H^+$	125.7±2.2	$H_4L^{18-} \rightleftharpoons H_3L^{19-} + H^+$	10.00	64.37
24	$3H_{22}L \rightleftharpoons (H_{22}L)_2H_{21}L^- + H^+$	~1.33			52.65

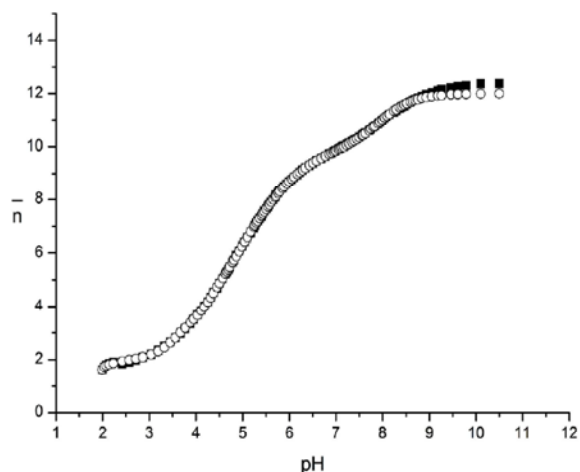


Fig. 3: Experimental (■) and calculated (○) dependencies of the Bjerrum function \bar{n} on the pH-value for the compound **III**.

Basing on mathematic simulation of experimental data, one may state that a second generation polyesterpolyacid (compound **I**) is characterized by blockwise ionization, with the even number of protons being mostly released.

Consider the ionization of hyperbranched polyester containing 22 propanoic acid fragments (compound **II**). Both experimental and theoretically calculated dependencies of the Bjerrum function on the pH-value show the only stage. The maximum Bjerrum function value is 19. Basing on the number of functional (carboxylic) groups, a stoichiometric matrix comprised 22 equilibria for the ionization of 22 carboxylic groups was obtained. Characterization of the experimental curve proved to be satisfactory. However, taking into consideration structural

similarity of compounds **I** and **II**, the equilibria of formation of dimers, trimers, tetramers and their ionized forms were introduced into the model. In this case, the correlation coefficient was 1.05% and the ionized trimer accumulated was detected. The most significant equilibria and forms are presented in Table 2.

Basing on mathematic simulation of experimental data, one may state that a third generation polyesterpolyacid (compound **II**) is characterized by blockwise ionization, while association is less characteristic.

Consider the ionization of hyperbranched polyester containing 12 acrylic acid fragments (compound **III**). Both experimental and theoretically calculated dependencies of the Bjerrum function on the pH-value show two slightly pronounced stages (Fig. 3). The maximum formation function value is 12. Basing on the number of functional (carboxylic) groups, a stoichiometric matrix comprised 12 equilibria for the ionization of 12 carboxylic groups was obtained. Characterization of the experimental curve proved to be unsatisfactory. Since carboxylic acids are characterized by self-association, the equilibria of formation of dimers, trimers, tetramers and their ionized forms were introduced into the model.

The correlation coefficient was 3.44%, with the content of trimers and tetramers accumulated being less than 0.05%. The most significant equilibria and forms are presented in Table 3.

Basing on mathematic simulation of experimental data, one may state that a second generation polyesterpolyacid (compound **III**) is characterized by stepwise ionization; with the even number of protons being mostly released.

Table 3: Parameters of ionization equilibria in solution of compound III ($V_{III}=5$ ml, $C_{III}=9.89 \times 10^{-3}$ M, $C_{NaOH}=0.0859$ M), $F_{min}=2.862$; $F_{pr}=0.968 \times 10^{-2}$; $R=3.441 \times 10^{-2}$.

#	Equilibria	pK_{gen}	Equilibria	pK_{step}	Share, %
1	$H_{12}L$		$H_{12}L$		4.097
2	$H_{12}L \rightleftharpoons H_{11}L + H^+$	1.35±0.09	$H_{12}L \rightleftharpoons H_{11}L + H^+$	1.35	17.95
3	$H_{12}L \rightleftharpoons H_{10}L^{2+} + 2H^+$	3.45±0.08	$H_{11}L \rightleftharpoons H_{10}L^{2+} + H^+$	2.10	17.19
4	$H_{12}L \rightleftharpoons H_9L^{3+} + 3H^+$	6.61±0.25	$H_{10}L^{2+} \rightleftharpoons H_9L^{3+} + H^+$	2.16	37.14
5	$H_{12}L \rightleftharpoons H_8L^{4+} + 4H^+$	11.68±0.09	$H_9L^{3+} \rightleftharpoons H_8L^{4+} + H^+$	5.07	44.24
6	$H_{12}L \rightleftharpoons H_7L^{5+} + 5H^+$	14.94±0.17	$H_8L^{4+} \rightleftharpoons H_7L^{5+} + H^+$	3.34	64.91
7	$H_{12}L \rightleftharpoons H_6L^{6+} + 6H^+$	20.48±0.36	$H_7L^{5+} \rightleftharpoons H_6L^{6+} + H^+$	5.54	10.14
8	$H_{12}L \rightleftharpoons H_5L^{7+} + 7H^+$	24.84±0.46	$H_6L^{6+} \rightleftharpoons H_5L^{7+} + H^+$	4.36	53.54
9	$H_{12}L \rightleftharpoons H_4L^{8+} + 8H^+$	30.55±0.10	$H_5L^{7+} \rightleftharpoons H_4L^{8+} + H^+$	5.71	28.20
10	$H_{12}L \rightleftharpoons H_3L^{9+} + 9H^+$	36.15±0.27	$H_4L^{8+} \rightleftharpoons H_3L^{9+} + H^+$	5.60	55.84
11	$H_{12}L \rightleftharpoons H_2L^{10+} + 10H^+$	42.70±0.25	$H_3L^{9+} \rightleftharpoons H_2L^{10+} + H^+$	6.55	67.5
12	$H_{12}L \rightleftharpoons HL^{11+} + 11H^+$	50.55±0.36	$H_2L^{10+} \rightleftharpoons HL^{11+} + H^+$	7.85	39.02
13	$H_{12}L \rightleftharpoons L^{12+} + 12H^+$	58.63±0.76	$HL^{11+} \rightleftharpoons L^{12+} + H^+$	8.09	99.58
15	$2H_{12}L \rightleftharpoons (H_{12}L)(H_8L)^{4+} + 4H^+$	3.73±0.06			70.41
16	$2H_{12}L \rightleftharpoons (H_{12}L)(H_6L)^{6+} + 6H^+$	11.02±0.99			31.94

CONCLUSIONS

Thus, the simulation of equilibria of hyperbranched functionalized polyesters ionized using the CPESP programme allows an adequate characterization of multistage ionization equilibria. The data obtained allow revealing the relationship between the parameters of equilibria of polyesterpolyacids ionized and their structure. The compounds were found to show the decreased self-association ability when going to greater generation and substitution degree. These data can be used for characterizing equilibria of complexation reactions of hyperbranched polyesterpolyacids and biophilic metal ions.

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