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LIGHT SCATTERING AND VISCOMETRY STUDY OF STAR-LIKE DEXTRAN-GRAFT-POLYACRYLAMIDE

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Abstract. Dextran-graft-Polyacrylamide copolymers (D-*g*-PAA) with a polysaccharide backbone having different molecular weights (M_w = 20 000 and M_w = 70 000) and with various number of PAA-grafts per one Dextran macromolecule have been synthesized. Light scattering and viscometry investigations have shown that the internal structure of D-g-PAA copolymers depends upon the distance between PAA-grafts. *Compactness* of D20-g-PAA copolymers is lower in comparison with D70-g-PAA samples due to different conformations of PAA grafted chains: a "mushroom" conformation for D70-g-PAA and a "worm-like" one for D20-g-PAA samples.

Keywords: dextran, polyacrylamide, graft copolymers, spherical brush.

1. Introduction

Polymers of non-linear architecture are extensively studied as novel types of controlled intramolecular structure substances. After some pioneering years of polymer-brush theory [1-6] and experimental work [7-9] in this field there is now a good evidence that such type of polymers possess unique properties due to their possibility to undergo the controlled structure transformations: change in shape, size, *etc*. This is not surprising, since the number of variable parameters becomes almost overwhelmingly large, namely, initial polymer architecture, average degree of polymerization, solubility properties, the solvent composition, distance between grafts, nature and flexibility of backbone and grafts, *etc*. All these factors can influence the formation of nanostructure and determine the final properties of such compounds. On the other hand, water-soluble synthetic and natural polymers have attracted great attention in the past decades due to their non-toxicity and environmental friendliness [10-12].

We have combined these two ideas, namely, to synthesize non-linear biohybrid water polymers of controlled nanostructure by grafting of synthetic polymer Polyacrylamide onto Polysaccharide backbone. It seems to be a promising approach to obtain new non-linear copolymers containing Polyacrylamide which is widely used in waste water treatment and medicine [13-15].

This study is aimed to investigate the effect of the distance between grafts on the internal structure of Dextran-*graft*-Polyacrylamide copolymers.

2. Experimental

2.1. Materials

Dextrans with different molecular weights were purchased from Serva (Sweden), the characteristics given by the manufacturer being M_w = 2·10^4 (designated as D20 throughout) and M_w = 7·10^4 (designated as D70 throughout). Self-exclusion chromatography (SEC) investigations in the laboratory of Institute Charles Sadron (see details below) have given M_w = 1.9·10^4 with M_w/M_n = 1.22 and M_w = 6.4·10^4 with M_w/M_n = 1.49, respectively. Cerium (IV) ammonium nitrate (CAN) from Aldrich was used as the initiator. Dextran samples and the ceric salts were used without further purification. Acrylamide (AA) was obtained from Reanal (Hungary), and was twice re-crystallized from chloroform and dried under vacuum at room temperature for 24 h. Two Polyacrylamide samples with M_w = 2.6·10^6 and M_w = 1.08·10^6 were used for comparative investigations.

2.2. Synthesis

Two series of Polyacrylamide grafted to Dextran backbone (D20 and D70), designated as D20-*g*-PAA and D70-*g*-PAA correspondingly, were synthesised by radical polymerization using Ce(IV)/HNO$_3$ redox system.

The mechanism of ceric ion initiation involves the formation of a chelate complex [16-17], which while decomposing generates free radical sites on the

polysaccharide backbone. These active free radicals trigger the growth of PAA chains in the presence of acrylic monomer. The average number of grafting sites per backbone molecule depends on the ratio of ceric ion

concentration to Dextran [18]. The ratio of mol Ce(IV) to mol Dextran was equal to 5, 10 and 15. The amount of monomer AA was kept the same for all syntheses. The reaction path is shown below:
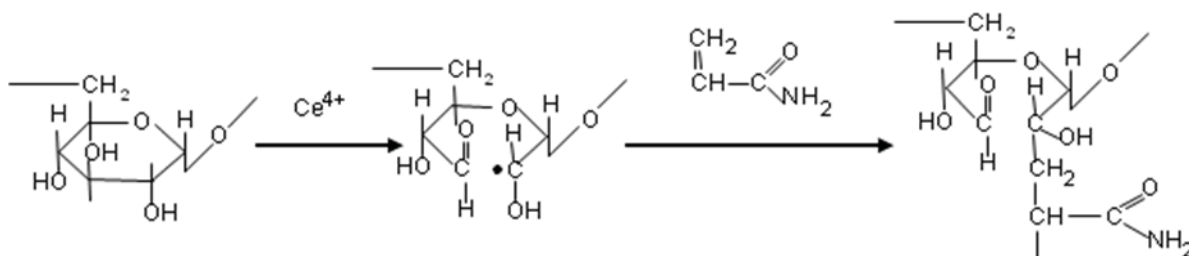
Calculated amount of Dextran (M_w = 20 000 and M_w = 70 000) was dissolved in 100 ml of distilled water. This solution was stirred while removal of the dissolved oxygen was achieved by bubbling a gentle flux of argon for about 20 min. A given amount of Ce(IV)/HNO$_3$ initiator (0.125 N HNO$_3$) was then added in such a way to have mol Ce(IV)/mol Dextran= N, where N is the number of grafts per backbone. The argon flux was left for another 2 min, then acrylamide monomer was added, and the polymerization proceeded under argon atmosphere for 24 h. Eventually, the copolymer was precipitated into an excess of acetone which gave chiefly two fractions: a fraction totally insoluble (the copolymer) and a remaining turbid suspension. The latter was discarded while the insoluble fraction was re-dissolved in water and finally freeze-dried.

2.3. Samples Characterization

2.3.1. Light scattering

The molecular parameters of D-g-PAA in a water solution were determined by the static light scattering (LS) experiments carried out by using SEMATECH apparatus with a laser source He-Ne of wavelength 632.8 nm and the scattering angle range between 30 and 150°. Light scattering results were analyzed in terms of the excess Rayleigh ratio $R(q)$ by using a classical Zimm-plot [19] which yields the weight-average molar mass M_w, the z-average radius of gyration R_z and the second virial coefficient A_2:

$$\frac{KC}{R(q)} = \frac{1}{M_w}\left[1 + \frac{q^2 R_z^2}{3}\right] + 2A_2C \qquad (1)$$

For vertically polarized incident light the optical constant K is given through:

$$K = \frac{4\pi^2 n^2}{N_A \lambda_o^4}\left(\frac{\partial n}{\partial C}\right)^2 \qquad (2)$$

where n is the refractive index of the solvent, λ_0 is the vacuum wavelength of the incident light beam and N_A is Avogadro's constant. The refractive index increments $\partial n/\partial C$ of the copolymers were measured by interferometry method. The samples of graft copolymers were dissolved in water at room temperature and the measurements were carried out after 24 h. All solutions and solvents were filtrated directly in the measuring cells using 0.45 µm Millipore filters.

2.3.2. Viscometry

The intrinsic viscosity was determined by viscometry measurements performed for a dilute solution at 298±0.1 K, using an Oswald type viscometer. The data were analyzed according to Huggins equation [20]:

$$\eta_{sp}/C = [\eta] + k_H[\eta]^2 C \qquad (3)$$

where η_{sp} is the specific viscosity, $[\eta]$ is the intrinsic viscosity and k_H is the Huggins constant. Extrapolation procedure from the data obtained for four concentrations of solutions was used to evaluate $[\eta]$.

2.3.3. Self-exclusion chromatography

SEC analysis was carried out by using a multidetection device consisting of a *LC-10AD SHIMADZU* pump (throughput 0.5 ml/min), an automatic injector *WISP 717+* from *WATERS*, 3 coupled *30cm-Shodex OH-pak* columns (803HQ, 804HQ, 806HQ), a multi-angle light scattering detector *DAWN F* from *WYATT TECHNOLOGY*, a differential refractometer *R410* from *WATERS*. The distilled water containing 0.1M NaNO$_3$ was used as an eluent. The solutions for SEC analysis (3 g/l) were prepared.

3. Results and Discussion

The commercial Dextrans used as the backbone for synthesizing the graft copolymers were characterized by SEC in water, because this method is a relevant tool for characterizing the polymers with a low molecular weight. The results obtained from SEC are gathered in

Table 1. The values of the weight-averaged molecular weights are in a rather good agreement with those provided by the manufacturer. It is known that in the water solution Dextran macromolecules possess conformation of coil [21] with cooperative systems of internal H-bonds. According to the value of M_w and R_z for D20 and D70 the Dextran macromolecule is quite compact in water and obviously the accessibility of Dextran macromolecules OH-groups for Ce(IV) ions can be different inside and outside the polysaccharide macrocoil.

Table 1

Molecular parameters (SEC) of individual Dextrans and PAA

Sample	$M_w \cdot 10^{-6}$	R_z, nm
D20	0.019	8
D70	0.064	15
PAA1	2.60	136
PAA2	1.08	72

In accordance with the synthesis conditions the copolymers of D20-*g*-PAA and D70-*g*-PAA series should have theoretically 5, 10 or 15 PAA-grafts per Dextran backbone, designated as D-*g*-PAA 1, D-*g*-PAA2 and D-*g*-PAA3 correspondingly. Graft spacing N_{Dex} (an average number of dextran residues between two grafts) has been assessed from the average Dextran molecular weight (M_{wDex}), the molecular weight of the monomer unit of Dextran (M_{Dex}) and the expected number of grafts per Dextran chains (N_{grafts}^{theo}):

$$N_{Dex} = \frac{M_{wDex}}{M_{Dex} N_{grafts}^{theo}} \qquad (4)$$

Theoretically D20-*g*-PAA samples have closer spacing between grafts in comparison with D70-*g*-PAA ones (Table 2) but for D20-*g*-PAA1 and D70-*g*-PAA3 the spacing between grafts is near the same.

Table 2

### Copolymers molecular parameters determined by LS and viscometry

Sample	$M_w \cdot 10^{-6}$	R_z, nm	$R_z^2/M_w \cdot 10^3$	$[\eta]$, dl/g	$C = 1/[\eta]$, g/dl	$Cont_{Dex}$	N_{Dex}
D20-*g*-PAA 1	3.65	152	6.33	3.4	0.29	0.6	25
D20-*g*-PAA 2	2.22	104	4.87	2.0	0.50	0.9	12
D20-*g*-PAA 3	1.08	59	3.22	1.2	0.83	1.9	8
D70-*g*-PAA 1	3.11	99	3.15	2.75	0.36	2.3	86
D70-*g*-PAA 2	2.43	78	2.50	2.1	0.48	2.9	43
D70-*g*-PAA 3	2.29	73	2.33	1.9	0.52	3.1	29

Molecular parameters of graft copolymers obtained by LS are shown in Table 2, a typical Zimm-plot is drawn in Fig. 1. According to the value of M_w and R_z for graft copolymers (Table 2) and individual Dextrans (Table 1) and also taking into account the content of polysaccharide component in copolymer we can assume that these copolymers are star-like ones. The content of polysaccharide component was calculated as:

$$Cont_{Dex} = \frac{M_{wDex}}{M_{copo}} \times 100\% \qquad (5)$$

where M_{wDex} – molecular weight of Dextran component in the copolymer; M_{copo} –molecular weight of graft copolymer obtained by LS.

All samples have high molecular weights but $M_{wD\text{-}g\text{-}PAA\ 1} > M_{wD\text{-}g\text{-}PAA\ 2} > M_{wD\text{-}g\text{-}PAA\ 3}$ for both series of copolymers with D20 and D70 backbone (Table 2). This is an expected result because CAN is an initiator of copolymerization and its interrupt agent concurrently. So, the increase of its amount in the system (for increase the grafts number) changes the balance of two opposite radical polymerization processes: growth of polymer chain and its rupture.
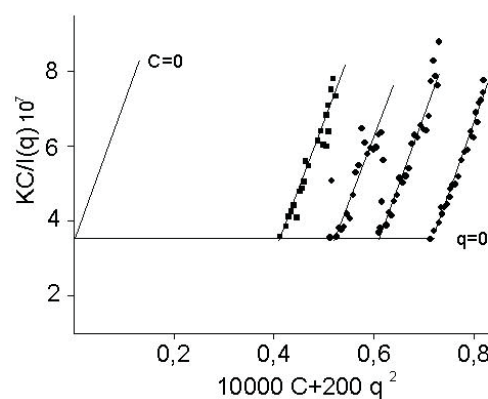
Fig. 1. Zimm-plot for D20-g-PAA1

Comparing the samples with D20 and D70 backbone (Table 2), it is revealed that M_w values are close to D-*g*-PAA1 and D-*g*-PAA2 ones, but for D-*g*-PAA3 the values of M_w drastically differ: $M_w = 1.08 \cdot 10^6$ for D20-*g*-PAA3 and $M_w = 2.29 \cdot 10^6$ for D70-*g*-PAA3. It confirms an assumption that the grafting process occurs mainly on the surface of Dextran macrocoil. R_z value is twice less for D20 in comparison with D70 (Table 1), hence, the amount of OH-groups on the coil surface is less for D20.

Obviously the amount of initiator and free OH-groups are commensurable only for D-g-PAA1 and D-g-PAA2 samples and the whole Ce(IV)-initiator is used for formation of a chelate complex [16-17].

Star-like copolymers D-g-PAA can be considered as spherical brushes [24] with Dextran core and PAA-corona. As it was predicted in the theoretical work the compactness of polymer brushes depends on the distance between grafts and their conformation [1, 24]. The factor of compactness that is expressed as R_z^2/M [23] has been analyzed for two series of copolymers and is represented in Table 2. When the value of R_z^2/M is lower, the compactness is higher. The compactness depends on the grafts number as well as the grafts conformation. While comparing the samples of D70-g-PAA and D20-g-PAA copolymers which are of close molecular mass we have established that the values of R_z^2/M for D20-g-PAA copolymers are higher (Table 2), therefore their compactness is lower. These data are in good agreement with our previous X-Ray results on a copolymer internal structure [22]. As it was reported for similar systems D20-g-PAA and D70-g-PAA with 6 long grafts the distance between grafts conditions influences the conformation of grafts: in case of D20-g-PAA the scattering curve closely resembles that of a worm-like chain. For D70-g-PAA the behaviour differs from that of a worm-like chain, although it is definitely not random, namely the PAA chains may be highly extended near their tethering point and recover a random conformation far from this point. Thus, the PAA grafts display a kind of "mushroom" conformation, which is more compact than the "worm-like" one (Fig. 2). The dependence of the compactness factor $vs.$ theoretical grafts number confirms that in D70-g-PAA copolymers PAA chains have the conformation close to the mushroom one as values of R_z^2/M_w are drastically less for these copolymers in comparison with D20-g-PAA ones (Fig. 3). However for D20-g-PAA3 and D70-g-PAA3 the factor of compactness becomes close. Thus, it confirms the theoretical prediction that compactness of polymer brushes depends on both factors simultaneously: the number of grafts and their conformations.
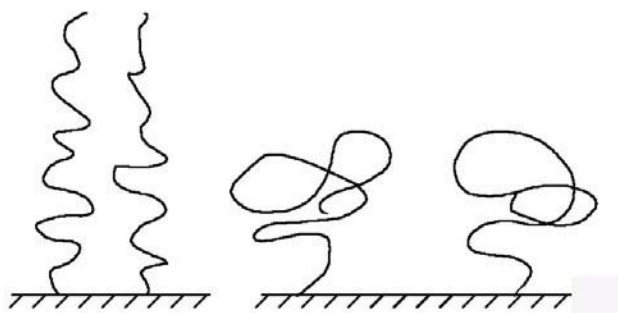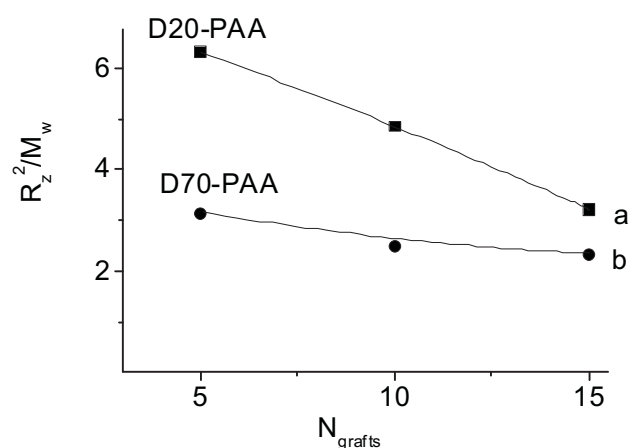

Fig. 2. Scheme of grafts conformation

Fig. 3. Factor of compactness $vs.$ the grafts number for D20-g-PAA (a) and D70-g-PAA (b)

Also, the values of the z-averaged radius of gyration, R_z, are higher for linear PAA of the similar molecular weight as graft copolymers, for example as for D70-g-PAA2 and PAA1; D20-PAA3 and PAA1 (Tables 1 and 2). It is not surprisingly, because the star-like structure of the copolymer should rather yield smaller radii of gyration, even if PAA chains are extended as for D20-PAA samples. These experimental results confirm the theoretical prediction of polymer brushes compactness [1].

The viscometric data are in good agreement with LS results, namely there is the correlation in changes of values of intrinsic viscosity [η] and R_z (Table 2, Figs. 4a and 4b) within both series (D70-g-PAA and D20-g-PAA). Viscometric results also confirm the conclusion about more compact structure for D70-g-PAA samples that can be caused only by mushroom conformation of grafted PAA-chains. However, first of all the viscometric data were used for critical concentration determination. Critical concentration C^* at which the polymer coils start to overlap is a very important parameter for investigation of macromolecules in solution. Generally, C^* is expressed as follows [1, 20]:

$$C^* = \frac{1}{[\eta]} \qquad (6)$$

It means that C^* is inversely proportional to the intrinsic viscosity [η], which is directly related to the macrocoil dimension or the segment density of the coil. The viscometric data are represented in Table 2 and Figs. 4a and 4b. The concentrations we used for samples characterization were low C^*; therefore the intermolecular interactions can be neglected. The form of Zimm plot also confirms this conclusion (Fig. 1). Thus, the molecular parameters of graft copolymers D-g-PAA characterize

properties of individual macromolecules in the water solution.

4. Conclusions

Two series of copolymers Dextran-graft-Polyacrylamide with different distance between PAA-grafts have been synthesised and studied by light scattering and viscometry methods. The samples are star-like copolymers and can be classified as the spherical brushes with Dextran core and Polyacrylamide corona [24]. LS and viscometry investigations have shown that the internal structure of D-g-PAA copolymers depends upon the distance between PAA-grafts. *Compactness* of D20-g-PAA copolymers is lower (higher value of R_z^2/M) in comparison with D70-g-PAA samples due to different conformation of PAA grafted chains: the "mushroom" conformation for D70-g-PAA and the "worm-like" one for D20-g-PAA samples.
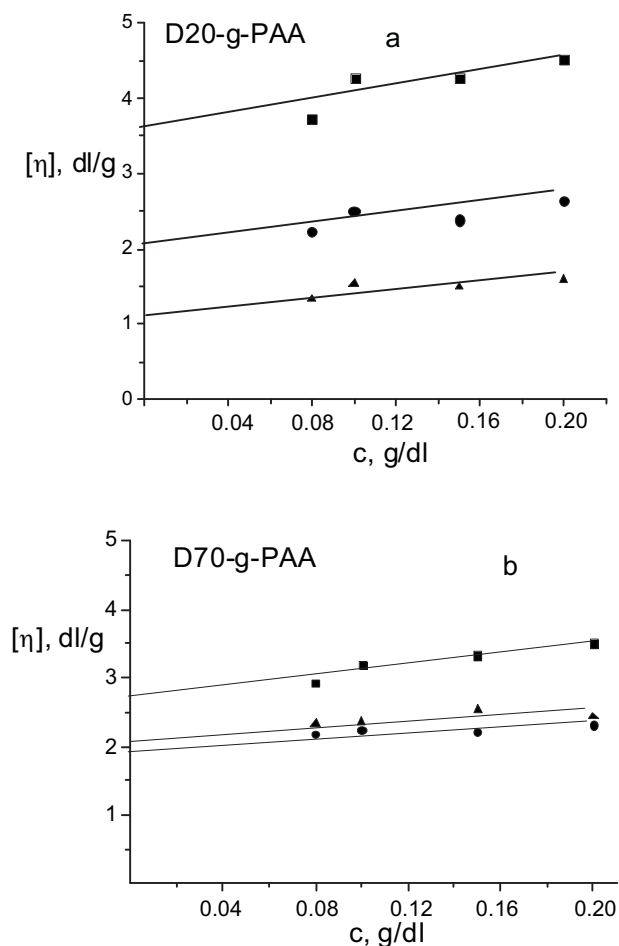

Fig. 4. Viscometric data for D-*g*-PAA copolymers in a water solution: for D20-*g*-PAA (a) and for D70-*g*-PAA (b)

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ДОСЛІДЖЕННЯ ЗІРКОПОДІБНИХ ПРИЩЕПЛЕНИХ КОПОЛІМЕРІВ ДЕКСТРАН-ПОЛІАКРИЛАМІД МЕТОДАМИ СВІТЛОРОЗСІЮВАННЯ ТА ВІСКОЗИМЕТРІЇ

Анотація. Синтезовано кополімери Декстран-Поліакриламід (Д-ПАА) з різною молекулярною масою основного полісахаридного ланцюга ($M_w = 20\,000$ та $M_w = 70\,000$) та різною кількістю щеплень на одну макромолекулу декстрану.

Методами віскозиметрії та світлорозсіювання показано, що внутрішньомолекулярна структура кополімерів Д-ПАА залежить від відстані між ПАА-щепленнями. Компактність Д20-ПАА кополімерів нижча у порівнянні зі зразками Д70-ПАА, що обумовлено різною конформацією прищеплених ПАА-ланцюгів ПАА: «грибоподібною» для Д70-ПАА та «черв'якоподібною» для Д20-ПАА.

Ключові слова: декстран, поліакриламід, прищеплені кополімери, сферичні щітки.