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Solution properties of dextran–polyacrylamide graft copolymers

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Abstract

Copolymers obtained by grafting polyacrylamide (PAA) onto polydextran (DEX) have been synthesised by ceric-ion-reduced redox initiation method. These copolymers have been characterized by light scattering, self-exclusion chromatography and viscometry in aqueous solutions. The short range molecular structure has been studied by small-angle X-ray scattering. From these results it is suggested that close to the anchoring point the grafted chains are extended while they take on a random conformation far from this point. A few investigations have been carried out in water/DMF (dimethyl formamide) mixtures. It is observed that the molecular weight depends strongly on the dimethyl formamide fraction. These results are discussed by contemplating the existence of PAA/DMF complexes.

Keywords: Graft copolymer; Dextran; Polyacrylamide

1. Introduction

Polymers possessing ligands capable of coordinating metal ions have received growing interest as they can de-pollute contaminated water and so prevent from accumulation of toxic metals, such as heavy metals, in human food. Water-soluble synthetic polymers and natural macromolecules are among the most efficient materials used as flocculants in the process of clarification of water either used in waterworks or rejected from industrial plants [1–4]. It is known that lignite-based sorbents, chitosan, corn biomass, modified polyacrylamide, and the like can remove heavy metals from water [2,5]. Synthetic polymers are much more efficient than natural polymers, yet, they are not shear resistant [1], a very important property when flocculants are used directly in water pipes and so submitted to a shearing flow. The advantages of natural polymers, such as polysaccharides, are their good stability under shear and also their biodegradability [1,6].

Several attempts have been made in the past decades to combine the best properties of both types of polymers by grafting synthetic polymers onto natural ones [7–11]. Many graft copolymers have been synthesized by grafting polyacrylamide (PAA) onto starch [1], sodium alginate [8], cellulose [9] and guar gum [11]. It was observed that such grafted copolymers are rather stable under shear, and thus can be efficient for treatment of industrial effluents.

So far, a systematic investigation of the molecular structure of such copolymers is missing although its knowledge is essential for a deep understanding of the mechanism involved in the capture of pollutants. Clearly, the copolymer microstructure will have a direct bearing upon the final properties. Knowledge of the molecular structure of graft copolymers and the way it is altered by modifying the chemical structure should allow one to have a better control of the size of the domains (cavities) acting as absorbent sites for heavy ions or small pollutants. This microstructure should be easily monitored through the relevant choice of chemical partners, the ratio of the main chain length to the grafts length, and the number of grafts.

This paper reports on the molecular characterization of such water-soluble, partly biodegradable graft copolymers possessing functional groups that are capable of forming donor–acceptor bonds.

The main chain consists of dextran, while the grafted chains consist of polyacrylamide (PAA). The choice of dextran relies

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on several aspects. First, dextrans of various molecular weights are commercially available. Second, the degree of branching of the dextrans can be as low as 0.5%, making them ideal molecular model for scientific studies. Third, dextran possesses high water solubility, is stable under mild acid and basic conditions, and contains a large number of hydroxyl groups for conjugation. The choice of polyacrylamide relies on the possibility of its chemical modification for obtaining anionic derivatives that show better flocculating behaviour than polyacrylamide itself [12].

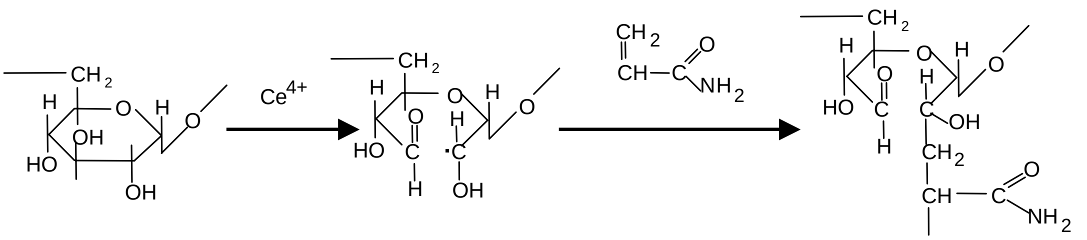
2. Experimental

2.1. Materials

Dextrans with different molecular weights were purchased from Serva (Sweden) whose characteristics given by the manufacturer are $M_w = 2\times10^4$ (designated as D20 throughout) and $M_w = 7\times10^4$ (designated as D70 throughout). SEC investigations in our laboratory (see details below) have given $M_w = 2.2\times10^4$ with $M_w/M_n = 1.22$ and $M_w = 7\times10^4$ with $M_w/M_n = 1.49$, respectively. Cerium (IV) ammonium nitrate (CAN) from Aldrich was used as initiator. Dextran samples and the ceric salts were used without further purification. Acrylamide (AA) was obtain from Reanal (Hungary), and was twice re-crystallized from chloroform and dried under vacuum at room temperature for 24 h. We used bidistilled water, while DMF was of analytical grade and so no further purification was performed.

2.2. Synthesis of dextran-graft–polyacrylamide copolymers

Ceric-ion-induced redox initiation method has been used for the synthesis of the graft copolymers. This redox process initiates free radical sites exclusively on the polysaccharide backbone, thus preventing from the formation of homopolymer (PAA) [13–15]. The mechanism of ceric ion initiation involves the formation of a chelate complex [13,14], which decomposes and 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 [13]. The suggested reaction path is shown below.



Calculated amount of dextran (2.5×10^{-3} mol) 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 (molCe(IV)/molDextran = 6) while the argon flux was left for another 10 min. A desired quantity of acrylamide monomer was added (0.2 mol), and then the polymerisation proceeded under argon atmosphere for 24 h. At the end of the reaction, the copolymer was precipitated into an excess of acetone. This gave essentially two fractions: a fraction totally insoluble, which we recovered, and a remaining turbid suspension, which was discarded. The insoluble fraction was re-dissolved in water and finally freeze-dried.

For this series of copolymers the ratio of molar concentrations of CAN and dextran was kept constant in the aim of obtaining copolymers with the same number of grafts [13].

The samples were freeze-dried after synthesis and always kept under vacuum for preventing them from hydrolysis. Potentiometric titration curves obtained for distilled water and for the copolymer solutions were the same whereas for controlled hydrolyzed samples with degree of hydrolysis 16% drastic changes of the titration curves were observed. We can, therefore, conclude that the degree of hydrolization of the PAA moiety in the nascent copolymer is virtually zero under the present experimental conditions.

2.3. Elemental analysis

Elemental analysis of the content of carbon and nitrogen has given values gathered in Table 1. As these samples are slightly hygroscopic, the measure of the oxygen and hydrogen contents are not relevant for determining the fraction of each polymer. Only the ratio of the percentage of nitrogen with respect to carbon's can yield some information about the sample. Indeed, by considering some water fraction (%W), one has

$$\%N = \frac{N_{\mathrm{PAA}}\times 14}{M_{\mathrm{Dex}} + N_{\mathrm{PAA}}\times 71 + \%W\times 18} \quad \text{and} \quad \%C = \frac{[0.4385\times M_{\mathrm{Dex}}] + N_{\mathrm{PAA}}\times 36}{M_{\mathrm{Dex}} + N_{\mathrm{PAA}}\times 71 + \%W\times 18} \tag{1}$$

where M_{Dex} is the dextran molecular weight, N_{PAA} the total number of PAA monomers. The ratio $W_{N/C} = \%N/\%C$ is independent of the oxygen content, and is written

$$W_{N/C} = \frac{N_{\mathrm{PAA}}\times 14}{[0.4385\times M_{\mathrm{Dex}}] + 36\times N_{\mathrm{PAA}}} \tag{2}$$

Table 1
Results of elemental analysis

Sample	%*N*	%*C*	X_{PAA} (%)
D20-*g*-PAA1	16.38±0.07	43.58±0.005	>96
D70-*g*-PAA1	15.49±0.01	43.22±0.03	>92

The weight fraction of PAA, X_{PAA}, in the copolymer is thus given through:

$$X_{\mathrm{PAA}}=\frac{31.13\times W_{N/C}}{14-4.87W_{N/C}} \tag{3}$$

Values of X_{PAA} are gathered in Table 1. These values should be taken as indicative, as the presence in the sample of other impurities containing carbon, such as non-reacted dextran chains, cannot be totally ignored. In principle, the global molecular weight can be calculated through

$$M_{\mathrm{w}}=\frac{M_{\mathrm{w}}^{\mathrm{dex}}}{1-X_{\mathrm{PAA}}} \tag{4}$$

where $M_{\mathrm{w}}^{\mathrm{dex}}$ is the weight averaged molecular weight of the dextran moiety.

2.4. 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, three coupled 30 cm-Shodex OH-pak columns (803HQ, 804HQ, 806HQ), a multi-angle light scattering detector DAWN F from WYATT TECHNOLOGY, a differential refractometer R410 from WATERS. Distilled water containing 0.1 M $NaNO_3$ was used as eluent. The solutions for the SEC analysis (3 g/L) were prepared.

2.5. Viscometry

Viscosity measurements were performed for dilute solution in a bath kept at 25±0.05 °C, using an Oswald type viscometer. The data were analyzed through:

$$\frac{\eta_{\mathrm{sp}}}{C}=[\eta]+k_{\mathrm{H}}[\eta]^2C+k_{\mathrm{H}}'[\eta]^3C^2 \tag{5}$$

where η_{sp} is the specific viscosity, $[\eta]$ the intrinsic viscosity and k_{H} and k_{H}' being Huggins constants.

2.6. Light scattering

The static light scattering experiments were carried out using commercial apparatus (SEMATECH) working with a laser source He–Ne of wavelength $\lambda=632.8$ nm. The scattering angle, θ, range investigated was between 30 and 150°. Light scattering results were analyzed in terms of the excess Rayleigh ratio $R(q)$ by using a classical Zimm-plot which yields the weight-average molar mass M_{w}, the z-average radius of gyration R_{z} and the second virial coefficient A_2:

$$\frac{KC}{R(q)}=\frac{1}{M_{\mathrm{w}}}\left[1+\frac{q^2R_{\mathrm{z}}^2}{3}\right]+2A_2C \tag{6}$$

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

$$K\frac{4\pi^2n^2}{N_{\mathrm{A}}\lambda_0^4}\left(\frac{\partial n}{\partial C}\right)^2 \tag{7}$$

where n is the refractive index of the solvent, λ_0 the vacuum wavelength of the incident light beam and N_{A} Avogadro's number. The refractive index increments $\partial n/\partial C$ for the copolymers were measured by interferometry method. The samples of graft copolymers were dissolved in water at room temperature while the measurements were carried out after 24 h to allow for complete, effective dissolution. Longer times were also occasionally used to check any evolution. All solutions and solvent were filtrated directly in the measuring cells using 0.45 μm millipore filters.

2.7. X-ray diffraction

The X-ray experiments were performed on beamline BM2 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The energy of the beam was 24 keV which corresponds to a wavelength of $\lambda=5.17\times10^{-2}$ nm. At the sample position the collimated beam was focused with a typical cross section of 0.1×0.3 mm^2. The scattered photons were collected onto a two-dimensional CCD detector developed by Princeton Instruments, presently Roper Scientific. Typical acquisition times were of about 50 s.

The sample-to-detector distance was set to $D=1.52$ m. Under these conditions, the scattering vectors range extended from $q=0.15$ to 3 nm^{-1}, with $q=(4\pi/\lambda)\sin(\theta/2)$, and where λ and θ are the wavelength and the scattering angle, respectively (further information are available on the following website http://www.esrf.fr).

The solutions, prepared beforehand in test tubes, were transferred into cylindrical thin-walled (≈0.1 mm thick) glass tubes of 3 mm inner diameter for X-ray measurements. Due to the small beam cross-section, these tubes are equivalent to containers with parallel walls. Such a geometry clearly simplifies data processing.

The data were radially regrouped so as to obtain a one-dimensional X-ray pattern out of the two-dimensional digitalized pictures. A silver behonate sample was used for calibrating the scale of transfer momenta q. The intensities were corrected for the detector response, dark current, sample transmission. The scattering curves for the copolymer were finally obtained by subtracting a spectrum from pure water through:

$$I_{\mathrm{copo}}(q)=I_{\mathrm{sample}}(q)-\left\lfloor\varphi I_{\mathrm{H_2O}}(q)\right\rfloor \tag{8}$$

where φ is the copolymer volume fraction.

3. Results and discussion

3.1. Molecular weight characterization in aqueous solutions

The commercial dextrans used for synthesizing the graft copolymer were characterized by SEC in water. The values found are very close to those provided by the manufacturer, namely $M_w = 2.2\times 10^4$ with $M_w/M_n = 1.23$ for D20 (value from manufacturer $M_w = 2\times 10^4$) and $M_w = 7\times 10^4$ with $M_w/M_n = 1.49$ for D70 (value from manufacturer $M_w = 7\times 10^4$).

The results obtained by light scattering on the two copolymers are reported in Table 2. A typical Zimm-plot is drawn in Fig. 1. As can be seen values of molecular weights are quite large. Surprisingly, the values of the z-averaged radius of gyration of the copolymers, R_z, are about the same as those measured for linear PAA with equivalent molecular weight for which the following relation has been established [16]:

$$R_z = 7.25\times 10^{-3} M_w^{0.64} \tag{9}$$

As the comb-like structure of the copolymer should rather yield smaller radii of gyration, one may surmise that PAA chains are more extended in the copolymer than usual. This assumption will received further support as will be detailed below.

Values of the second virial coefficient values A_2 are rather high for such molecular weights, and, therefore, suggest that water behaves as a good solvent.

The results obtained from SEC are shown in Fig. 2, and the data are gathered in Table 2. The values of the weight-averaged molecular weights are in rather good agreement with those derived from light scattering. This shows that SEC in water is a relevant tool for characterizing these copolymers, and easier to use than light scattering. Also, SEC indicates that these samples possess relatively low molecular weight polydispersity.

It is worth emphasizing that the molecular weight one would deduce from elemental analysis, from the values of X_{PAA} and M_{Dex} (relation 4), is typically one order of magnitude lower than those measured by light scattering and SEC. As stressed above, some impurities containing carbon may biased the value of X_{PAA} to the extent of lowering it subsequently. With copolymer molecular weights around 5×10^6, X_{PAA} should be close to 99% as can be shown from relation 4. Most probably, the excess of carbon originates in the presence of dextran chains that have poorly or not reacted at all with cerium ammonium nitrate, and so not triggered the growth of PAA chains required for producing the copolymer. Indeed, it suffices to double the amount of dextran in the final product, namely increasing the dextran fraction from 0.3 to 0.6%, for decreasing the value of X_{PAA} of a few percent. To be sure, this very small excess of dextran cannot be detected by SEC. Clearly, elemental analysis is of no use for determining the total copolymer molecular weight while knowing the molecular weight of the dextran moiety.

Attempts to measure the PAA grafts molecular weight by degradation of the dextran backbone, and recovery of the PAA grafts have failed. Periodate oxidation [17–19] and acid hydrolysis [20] of the glucose units were used for degradating the dextran polymer. Viscosity measurements of the products of the oxidation process differed little from those of the starting copolymer, which presumably indicates that the procedure is not efficient with these systems. Conversely, acid hydrolysis led to poorly-soluble fractions which suggests the occurrence of cross-linking between PAA chains.

Still, as the desired number of graft per dextran chains was fixed at $N_{PAA} = 6$, we surmise, in view of the molecular weight measured for the copolymers, that the PAA graft average molecular weight is somewhere between $M_{PAA} = 5\times 10^5$ and 10^6, which was the value aimed at.

3.2. Molecular structure in aqueous solutions

The molecular structure has been examined by small-angle X-ray scattering. Results are drawn in Figs. 3 and 4 by means of Kratky representation ($q^2I(q)$ vs q). Fig. 3 shows that the intensity depends little upon the polymer concentration, which implies that intramolecular scattering can be ignored in the explored q-range, and correspondingly that one is probing the copolymer structure only. Interestingly, Figs. 3 and 4 point out the significant departure from the $1/q^2$ behaviour, but also the absence of $1/q^4$ behaviour. This indicates that one is actually probing the PAA chains local structure.

In the case of D20-PAA1 the scattering curve (Fig. 3) resembles closely that of a worm-like chain, which reads for $ql_p > 1$, where l_p is the persistence length [21]:

$$q^2 I(q) \propto \frac{\pi q}{l_p} + \frac{2}{3l_p^2} \tag{10}$$

A linear variation is thus expected in this q-range.

For $ql_p < 1$, the scattering curve is written [22]:

$$P_1(q) = \frac{2}{X}(\exp - X - 1 + X) + \frac{2l_p}{15L}\left[4 + \frac{7}{X} - \left(11 + \frac{7}{X}\right)\exp - X\right] \tag{11}$$

where $X = q^2 l_p L/3$, L being the length of the chain. The intercept between both regimes gives a scattering vector q^*

Table 2
Molecular parameters of graft copolymers determined by light scattering and viscometry methods in water

Sample	$\partial n/\partial C$	M_w (LS)	M_w (SEC)	M_w/M_n (SEC)	A_2 (cm^3/g) (LS)	R_z (nm) (LS)	$[\eta]$ (dl/g)
D20-*g*-PAA1	0.156	6.9×10^6	5.2×10^6	1.81	3.3×10^{-4}	182	8.5
D70-*g*-PAA1	0.172	4.7×10^6	3.2×10^6	1.65	3.7×10^{-4}	168	8.3

LS, light scattering; SEC, self-exclusion chromatography.

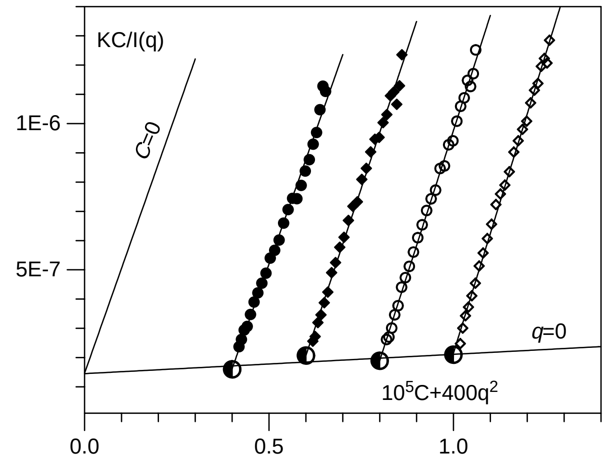


Fig. 1. Typical Zimm-plot obtained in aqueous solutions of D20-PAA1.

which can be calculated from Des Cloizeaux's equations [21] and is written:

$$q^* = \frac{16}{3\pi l_p} \tag{12}$$

By applying the worm-like chain model to the graft of D20-PAA1, one would, therefore, have a persistence length of $l_p \approx 2.7$ nm, namely about three times larger than the usual value of the unperturbed state of flexible polymers.

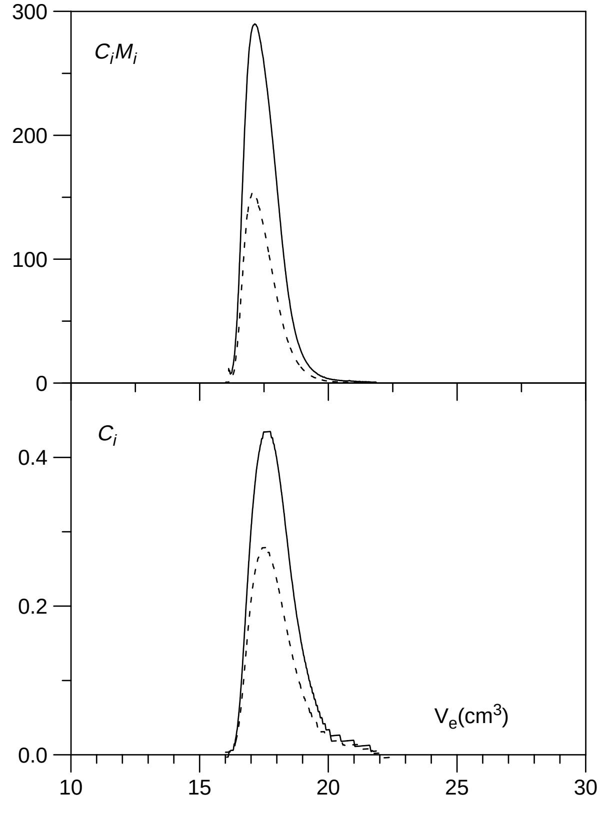


Fig. 2. SEC data for D20PAA1 (dotted line) and D70PAA1 (solid line). Upper curve C_iM_i vs the elution volume V_e, lower curve C_i vs V_e.

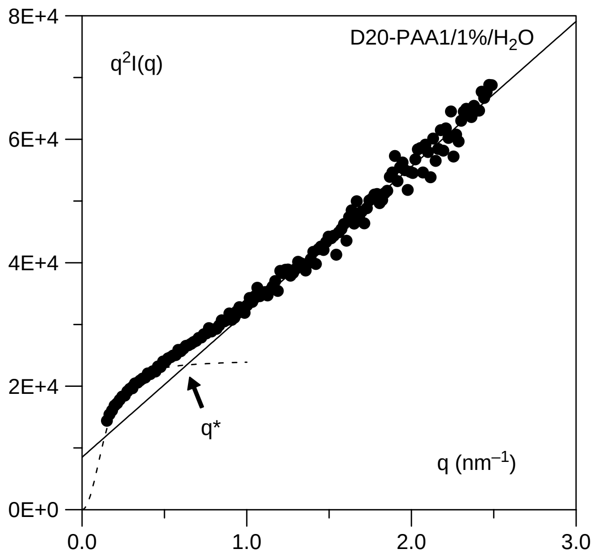


Fig. 3. X-ray small angle scattering curve plotted by means of a Kratky-plot $q^2I(q)$ vs q for D20-PAA1 copolymer in water solutions $C_{\text{copo}} = 0.01$ g/cm^3. The solid line stands for rod-like behaviour ($ql_p > 1$) and the dotted line for the flexible chain behaviour ($ql_p < 1$) calculated from relation 11.

Note that another model where the chain would be highly extended close to its tethering point and more random far from it could also fit the experimental data (Fig. 5). Schematically the space available to one graft is a cone whose solid angle is related to the distance between adjacent grafts, namely the larger the distance, the larger the cone solid angle. Typically, the intensity can be qualitatively written:

$$I(q) \propto \frac{A}{q^2}X + \frac{B}{q}(1-X) \tag{13}$$

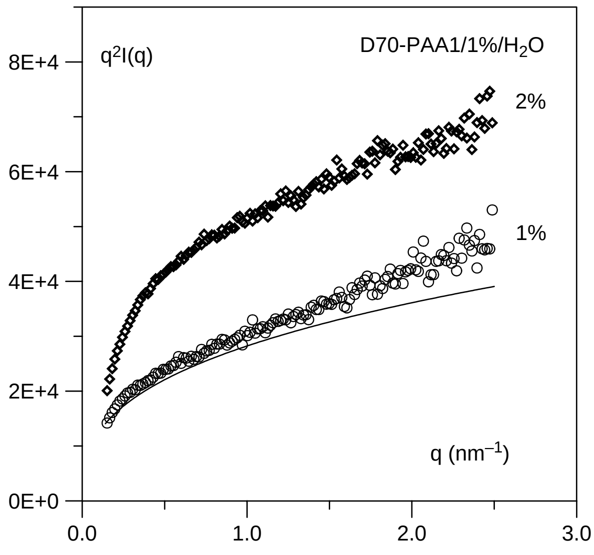


Fig. 4. X-ray small angle scattering curve plotted by means of a Kratky-plot $q^2I(q)$ vs q for D70-PAA1 copolymer in water solutions. Upper curve $C_{\text{copo}} = 0.02$ g/cm^3, lower curve $C_{\text{copo}} = 0.01$ g/cm^3. The solid line has been obtained after rescaling the upper curve by the ratio of concentrations and after spline smoothing of the resulting curve. This highlights the absence of significant concentration effect.

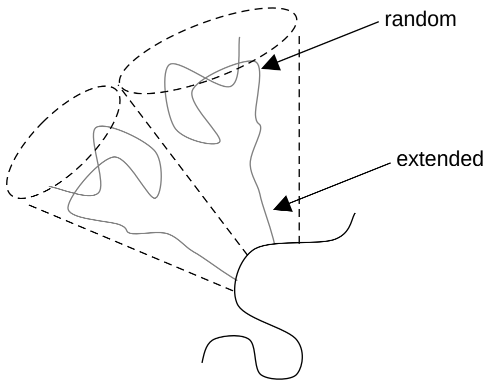


Fig. 5. Schematic model of the copolymer structure emphasizing the PAA chains extension near the anchoring point on the dextran backbone.

where X is the fraction of the purely-random part. This would then give in a Kratky-representation:

$$q^2 I(q) \propto AX + (1-X)Bq \quad (14)$$

This relation shows that a $1/q$ behaviour is expected at large q with a value of after extrapolation to $q=0$ which depends on the fraction of the purely random part.

The scattering curve for D70-PAA1, should rather be fitted with relation 14 (Fig. 4). The term obtained after extrapolation of the $1/q$ behaviour to $q=0$ suggest a larger fraction of the purely-random part. This suggests that the PAA chains recover more rapidly their randomness that those of D20-PAA1 may be extended near their tethering point but recover rapidly a random conformation far from this point, as is sketched in the molecular model of Fig. 5.

These results together with the molecular model suggest that the copolymer structure is rather 'swollen', due to the extension of the PAA chains. This statement is in agreement with the high values of radii of gyration found by light scattering. In any case, the copolymer structure is not compact at all as opposed to what has been surmised for other systems.

It is worth emphasizing that the model of Fig. 4 considers basically the same approach as that developed by Frederickson [23] for complexes formed by surfactants interacting with flexible polymer chains. Frederickson has theoretically shown that when the number of surfactant molecules anchored to the polymer exceeds a certain critical value their conformation undergoes significant extension. The only difference is that the PAA chains are definitely much longer than surfactant molecules. As predicted from the theory, the closest the PAA chains on the dextane backbone, the more extended they are.

3.3. Preliminary investigations in binary solvents

As these copolymers are eventually intended for capturing pollutants, tests have been made with binary systems, namely water containing increasing fractions of dimethyl formamide (DMF). As long as the fraction of DMF remains lower than 30% solutions can be obtained. Beyond this fraction, precipitation occurs. Note that the copolymers are totally insoluble in pure DMF. A viscometric study has been carried out, and results are shown in Figs. 6 and 7. While in pure water a linear variation is seen with a Huggins coefficient slightly negative, a strong upturn is observed in the binary solvents at low dilutions, an effect far larger than the experimental uncertainties. Also, the higher the DMF content, the stronger the upturn. This effect is reminiscent of a 'polyelectrolyte effect', although no dissociation can occur that would be liable to make electric charges appear as that taking place in polylectrolytes.

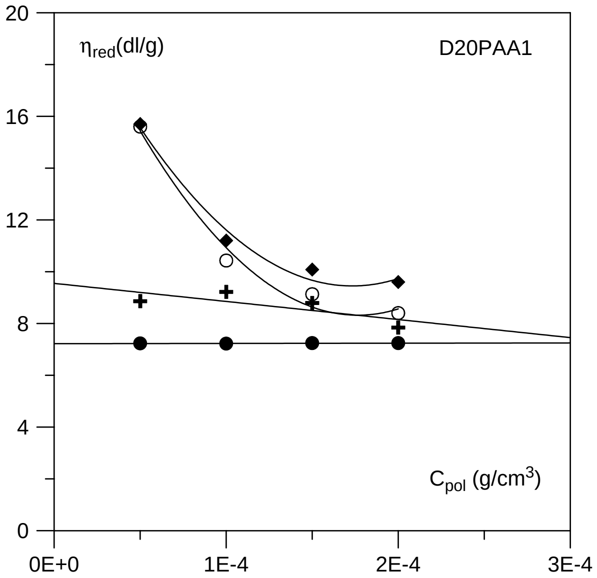


Fig. 6. Variation of the reduced viscosity as a function of polymer concentration for D20-PAA1 in different mixtures of binary solvent water+DMF. (●)=100% water, (+) 90%water+10%DMF; (○) 80%water+20%DMF; (♦) 70%water+30%DMF. For the last two mixtures polynomial fitting with degree 2 is used.

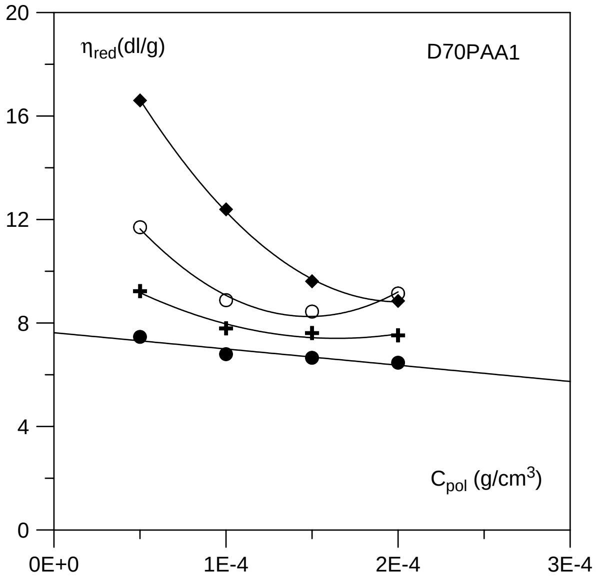


Fig. 7. Variation of the reduced viscosity as a function of polymer concentration for D70-PAA1 in different mixtures of binary solvent water+DMF. (●)=100% water, (+) 90%water+10%DMF; (○) 80%water+20%DMF; (♦) 70%water+30%DMF. For the last two mixtures polynomial fitting with degree 2 is used.

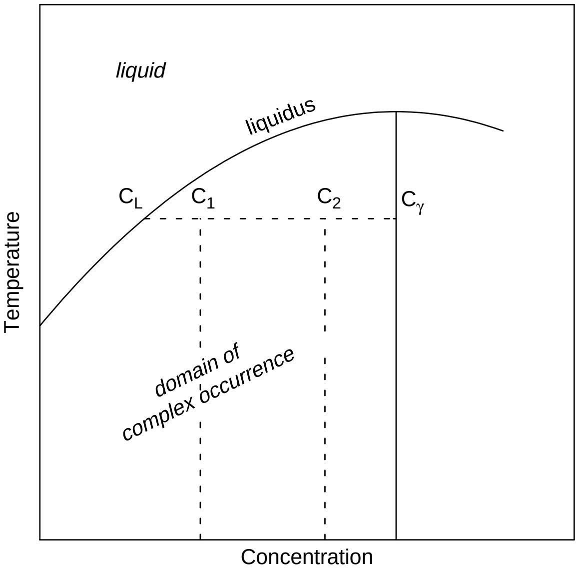


Fig. 8. A hypothetical temperature-concentration phase diagram standing for the formation of a polymer–solvent complex whose stoichiometric composition is C_γ. Decreasing the polymer concentration entails two effects: (i) the complex melts at lower temperature, and (ii) the fraction of complex with respect to polymer solution decreases. This is described by the lever rule derived by Gibbs: at a concentration C_2 the fraction of complex is $X_2=(C_2-C_L)/(C_\gamma-C_L)$ while at a concentration C_1 the same is $X_1=(C_1-C_L)/(C_\gamma-C_L)$. Clearly, dilution from C_2 to C_1 entails $X_1<X_2$.

Another explanation can be put forward which rather considers the formation of a ternary complex, something already contemplated and demonstrated for agarose gels [24]. DMF can interact strongly with water so as to form complexes. This complex formation essentially occurs through electrostactic interactions: positive ‘fractional’ charges appear on the CH_3 which interact with the negative fractional charges occurring on the water molecules. Interestingly, when only hydrogen bonds are involved, as with formamide, no complex is formed with this solvent and water [25]. Therefore, DMF is liable to interact with the C=O groups, that are negatively-charged, through electrostatic interactions. We suspect that a ternary complex is formed in this fashion between water, DMF and PAA chains which entails aggregation between copolymer molecules as has been shown to occur with agarose gels in the same binary solvents. This aggregation may occur through interdigitation of the copolymer molecules (a simple picture would be to consider interdigitation of bottle-brushes). If so, as is detailed in the legend of the hypothetical phase diagram of Fig. 8, the fraction of complex, that is the fraction of copolymer molecules aggregated thanks to this complexation effect, will decrease with the dilution. The theoretical expression of the intrinsic viscosity is needed to explain the effect further. $[\eta]$ is expressed through [26]:

$$[\eta] \propto \frac{R_g^2 \times R_H}{M} \tag{15}$$

where R_g^2 is the mean-square radius of gyration, R_H the hydrodynamic radius and M the molecular weight of the particles.

If dilution effectively entails gradual melting (disappearance) of the complex, then the molecular weight of the particles is to decrease significantly. Meanwhile, if complexation has occurred through an interdigitation process, then the size of the particles may not change drastically unlike their molecular weight. Under these conditions, $[\eta]$ is likely to increase significantly giving rise to a ‘pseudo’ polyelectrolyte effect. Note that the type of explanation developed here may account for the same effect observed for polyelectrolyte/surfactant complexes in solvents of lower dielectric constant than water where no dissociation is likely to occur [27].

Small-angle X-rays experiments will be carried out in a near future in order to investigate the short range structure of the copolymers which should be significantly altered if the complexation-driven aggregation of the copolymers takes place through interdigitation.

4. Concluding remarks

In this paper, we have reported on a study of aqueous solutions of graft copolymers. We have observed that the PAA grafted chains are significantly extended, and that the degree of ‘extension’ depends on the distance between grafts. This observation is consistent with Frederickson theory, but in contradistinction to results obtained on similar systems [28] for which the occurrence of intra complexation (interaction of PAA chains with the copolymer backbone) is supposed.

Also, investigations into the intrinsic viscosity of the copolymers in binary aqueous solutions water+DMF, a ‘polyelectrolyte behaviour’ has been observed. We suspect that this effect is due to the gradual melting of a ternary complex copolymer/water/DMF upon dilution, and is foreign to any charge effect.

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