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Hybrid Hydrogels Obtained by the Copolymerization of Acrylamide with Aggregates of Methacryloyl Derivatives of Polyoxotungstates. A Comparison with Polyacrylamide Hydrogels with Trapped Aggregates[†]

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ABSTRACT: The synthesis and the swelling properties of two types of hybrid hydrogels have been studied to point out the contribution of cross-linking organic−inorganic aggregates to the network formation and the water absorption. The first type consists of polyacrylamide hydrogels with embedded polyoxotungstates. The second one has been obtained by radical polymerization of acrylamide in the presence of copolymerizable polyoxotungstates above their critical aggregation concentration. As recently reported for polyacrylamide hydrogels with trapped rods, the incorporation of such polyelectrolytes in a neutral network enhances the ability of the hydrogel to absord water. The same observation holds for polyacrylamide hydrogels with trapped polyoxotungstate aggregates. As polymerizable tetrafunctional polyoxotungstates and acrylamide were copolymerized, aggregate-containing hydrogels were obtained. Their swelling properties were found to be in the low range of those of superabsorbent materials and are discussed in relation to the presence of aggregated species.

Introduction

Because of their “value-adding properties”,[1] the entrapment of polyoxotungstates in polymer matrices and the applications of the resulting hybrid materials have been extensively studied.[2] On the other hand, the incorporation by *covalent links* has never been reported although, surprisingly, clusters with polymerizable functionalities have been obtained for several years.[3] However, to a larger extent, Sanchez *et al.* reported several strategies to design hybrid organic−inorganic materials such as polyhedral oligomeric silsesquioxanes, for instance.[4]

We recently described the synthesis and the swelling properties of hybrid networks made of poly(ethyl methacrylate) chains covalently cross-linked by CH_3CN-soluble polyoxotungstates, which was the first example in this field.[5] Since then, the preparation of the water-soluble polymerizable polyanion $[\gamma\text{-SiW}_{10}O_{36}(CH_2{=}C(CH_3)CO_2(CH_2)_3\ SiO)_4]^{4-}$ (POM_1; Figure 1a) has offered the possibility to synthesize hydrogels.[6] In the present paper, the synthesis of new hybrid hydrogels from acrylamide (AAm) and POM_1 as cross-linker is described with emphasis on the contribution of the POM_1 aggregates to the formation and the swelling properties of the networks (type I hydrogels). To appreciate the polyelectrolyte effect of the aggregates, type II hydrogels were synthesized from AAm, *N,N′*-methylenebis(acrylamide) (BAAm), and $[\gamma\text{-SiW}_{10}O_{36}(PhSiO)_4]^{4-}$ (POM_2; Figure 1b), which is a nonpolymerizable polyanion. In this respect, type II hydrogels belong to the same family as that defined by Philipova *et al.*[7] On the other hand, since POM_1 participates directly in the covalent structure of the networks (type I hydrogels) as both a molecular cross-linker and a cross-linking aggregated species, it constitutes a new class of hydrogels where the hybrid cross-linker acts also as a nanometric mineral filler and a polyelectrolyte.

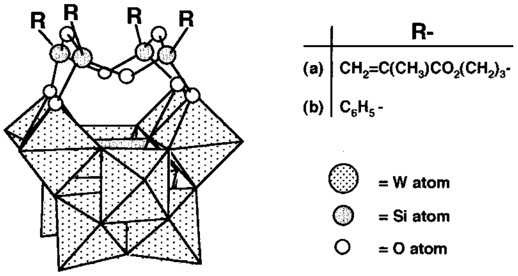

Figure 1. Schematic drawing of the hybrid polyanions: (a) for $R = CH_2{=}C(CH_3)CO_2(CH_2)_3$, the tetrafunctional polyoxotunstate (POM_1) involved in the formation of the hydrogels, and (b) for $R = C_6H_5$, the nonpolymerizable polyanion (POM_2).

Experimental Section

Synthesis and Characterization of the Polymerizable Polyoxotungstate as a Sodium Salt (POM_1). 3-Methacryloxypropyltrimethoxysilane ($CH_2{=}C(Me)C(O)OPrSi(OMe)_3$) (0.94 mL, 4 mmol) was added to a suspension of $K_8[\gamma\text{-SiW}_{10}O_{36}]\cdot 8H_2O$[8] (3 g, 1 mmol) in 50 mL of a CH_3CN/H_2O mixture (60/40 v/v). The reaction medium was acidified with 0.4 mL of a 12 M solution of hydrochloric acid and stirred for 4 h. The acidic compound recovered after evaporation of the solvents was dissolved in deionized water, and the solution was adjusted to pH 5.4 with an aqueous solution of NaOH. Water was evaporated, and the white residue (POM_1) washed with EtOH and then acetone and dried under vacuum. Yield: 2.9 g (91%). Anal. Calcd for $C_{28}H_{45.1}Na_{2.9}Si_5W_{10}O_{48}$: C, 10.52; H, 1.43; Na, 2.09; Si, 4.39; W, 57.54; O, 24.02. Found: C, 11.04;

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Table 1. Degree of Swelling Of Type I Hydrogels as a Function of the Initial Acrylamide (AAm) and Tetrafunctionalized Polyanion (POM_1) Concentrations

gel sample	$[AAm]_0$ ($mol \cdot L^{-1}$)	$[POM_1]_0$ ($mol \cdot L^{-1}$) $\times 10^2$	x_{POM1}[a] $\times 10^2$	$(m - m_0)/m_0$ (g/g)[b]
1	1.41	2.8	1.9	36
2	1.06	2.1	1.9	108
3	0.84	1.7	1.9	138
4	0.60	1.2	2.0	196
5	0.53	1.0	1.9	268
6	0.84	2.7	3.1	59
7	0.84	4.2	4.8	28
8	0.84	8.4	9.1	10

[a] Molar fraction of the tetrafunctionalized polyanion (POM_1) in the feed. [b] m and m_0 correspond to the weights of the wet and the dry gels, respectively.

H, 1.48; Na, 2.07; Si, 4.42; W, 57.88; O, 23.11. ^1H NMR (D_2O): $\delta = 6.01$ and 5.50 (d, 1H, vinylic protons), 4.07 (m, 2H, $-O-CH_2-$), 1.86 (s, 3H, $(H_3C)-C$), 1.70 (m, 2H, $-CH_2$-), 0.65 (t, 3H, $-CH_2-Si$) ppm. ^1H NMR (D_2O): $\delta = 6.01$ (d, 1H, HC=), 5.50 (d, 1H, HC=), 4.07 (m, 2H, $-O-CH_2-$), 1.86 (s, 3H, $(H_3C)-C$), 1.70 (m, 2H, $-CH_2-$), 0.65 (t, 3H, $-CH_2-Si$) ppm. IR (cm^{-1}): 1714 [vs, ν(CO)], 1636 [m, ν(C=C)], 1324 [m, δ(CH)], 1300 [m, δ(COR)], 1200 [vs, δ(CO)], 1170 [s, ν(SiC)], 1108 [vs, ν(SiO)], 1081 [vs, ν(SiO)], 1058 [vs, ν(SiO)], 989 [vw, ν(SiO)], 963 [vs, $\nu(WO_{ter})$], 925 [vs, ν(WO)], 902 [vs, ν(WO)], 868 [vs, ν(WO)], 820 [vs, ν(WO)], 748 [vs, ν(WO)], 562 [vw, δ(SiO)], 538 [vw, δ(SiO)], 412 [vw, δ(WO)], 368 [vw, δ(WO)]. The critical aggregation concentration (CAC) and the surface tension of a water solution of POM_1 were determined at 25 °C and are equal to 4.3×10^{-4} $mol \cdot L^{-1}$ and 43.5 $mN \cdot m^{-1}$ at the CAC, respectively. The surface area of its polar head is equal to 139 $Å^2$.

Synthesis and Characterization of the Nonpolymerizable Polyoxotungstate as a Sodium Salt (POM_2). $[\gamma\text{-}SiW_{10}O_{36}(PhSiO)_4]^{4-}$ (POM_2) was synthesized from $K_8[\gamma\text{-}SiW_{10}O_{36}] \cdot 8H_2O$ and $PhSi(OMe)_3$ following the procedure described for the preparation of POM_1. ^1H NMR (CD_3CN): $\delta = 7.8$ (d, 1H), 7.3 (d, 2H), 7.1 (d, 2H) ppm. IR (cm^{-1}) (superscript a, from $\{RSiO_3\}$; superscript b, from $\{SiO_4\}$): 1135 [vs, $\nu(SiC)^a$], 1109 [vs, $\nu(SiO)^a$], 1084 [vs, $\nu(SiO)^a$], 1054 [vs, $\nu(SiO)^a$], 998 [vw, $\nu(SiO)^b$], 966 [vs, $\nu(WO^{ter})$], 911 [vs, ν(WO)], 905 [vs, ν(WO)], 871 [vs, ν(WO)], 816 [vs, ν(WO)], 739 [vs, ν(WO)], 697 [vs, δ(C=CH)], 551 [vw, δ(SiO)], 539 [vw, δ(SiO)], 412 [vw, δ(WO)], 359 [vw, δ(WO)].

Synthesis of the Hydrogels. POM_1 and acrylamide were dissolved in water in appropriate amounts depending on the required molar fraction of the cross-linker x_{POM} (gels **1**−**8**, Table 1). Potassium persulfate (1 mol % with respect to acrylamide) was introduced once the solution was degassed with argon. The reaction mixture was heated at 70 °C for 2 h. The so-called type I hydrogels were allowed to swell at room temperature to equilibrium. Type II hydrogels were prepared following the same procedure: AAm and BAAm were copolymerized in the presence of POM_2 (gels **9**−**18**, Table 2). BAAm cross-linked polyacrylamide gels were also synthesized in the absence of POM_2 (gels **19**−**25**, Table 2).

Gel Swelling. The degree of swelling of the gel samples was determined at the swelling equilibrium at 25 °C with the degree of swelling characterized by $(m - m_0)/m_0$, where m and m_0 are the weights of the swollen and dry gels, respectively.

Instrumental Methods. The reagents and the solvents were purchased from Aldrich and used as received. The IR spectra (4000−250 cm^{-1}) were recorded on a Bio-Rad FTS 165 IR FT spectrometer with compounds and dried gels sampled in KBr pellets. ^1H NMR (300 MHz) spectra were recorded at room temperature in 5 mm outside diameter tubes on a Bruker AC 300 spectrometer equipped with a QNP probehead. The chemical shifts are given with respect to $SiMe_4$. Transmission electron microscopy (TEM) was performed using a JEOL 100 CX2 microscope from droplets of solution and from microcoated hydrogel samples deposited on a grid. Surface tension was measured on a Krun KT 10 tensiometer.

Table 2. Degree of Swelling of Type II Hydrogels as a Function of the Initial Bisacrylamide (BAAm) and Nonpolymerizable Polyanion (POM_2) Concentrations[a]

gel sample	$[BAAm]_0$ $\times 10^2$ ($mol \cdot L^{-1}$)	$[POM_2]_0$ $\times 10^2$ [b] ($mol \cdot L^{-1}$)	$(m - m_0)/m_0$ (g/g)
9	0.22	0	69
10	0.45	0	52
11	0.60	0	43
12	0.88	0	37
13	2.0	0	22
14	5.0	0	19
15	10.0	0	18
16	0.20	1.2	146
17	0.35	1.2	118
18	0.46	1.2	98
19	0.65	1.2	68
20	1.7	1.2	39
21	4.2	1.2	25
22	8.4	1.2	13
23	0.68	0.21	55
24	0.68	0.51	61
25	0.68	0.84	66

[a] $[AAm]_0 = 0.84$ $mol \cdot L^{-1}$. [b] POM_2 is a bifunctionalized but nonpolymerizable polyoxotungstate (see the Experimental Section for details).

Results and Discussion

Characterization of Type I Hydrogels. Type I hydrogels were obtained from acrylamide solutions (0.53−1.41 $mol \cdot L^{-1}$) containing POM_1 at concentrations much higher than the CAC (Table 1; CAC = 4.3×10^{-4} $mol \cdot L^{-1}$ in water at 25 °C). Aggregates were observed in the starting solutions (Figure 2a) and inside the dry gels (Figure 2b).

As qualitatively shown by transmission electron microscopy (Figure 2a), *ca*. 7 nm diameter spherical aggregates are homogeneously dispersed in the starting solution. Their size distribution seems not to be very large. Geometric packing considerations (based on the length l_c and the volume v of the alkyl chain and the optimal headgroup area a_0 of POM_1) are consistent with the existence of spherical bilayers (vesicles) whose smallest diameter is in the 4−6 nm range, with the corresponding aggregation number between 30 and 120 polyanions. The analysis by small-angle X-ray scattering should bring more information on the structure of these aggregates and will be published elsewhere.

Inside the gels in the dry state (Figure 2b), the shape of the aggregates is much more poorly defined and the size distribution is wider. In addition, 30 nm diameter aggregates can be observed so that the morphology of the dispersed phase differs from that observed in the starting solution.

The modification can be ascribed to the influence of the cross-linking process, to the temperature increase from 25 to 70 °C, and to the drying of the hydrogel (80 °C, atmospheric pressure). The vesicles probably fused during the course of these three steps, leading to the formation of larger structures.

^1H NMR analysis of the gels in the D_2O-swollen state showed that the signals characteristic of the vinylic protons are no longer present in the gel samples. This indicates at least that all the double bonds of the *free* polyoxotungstates have been consumed during the copolymerization or that all unreacted *free* polyanions have diffused out of the gel during the swelling.

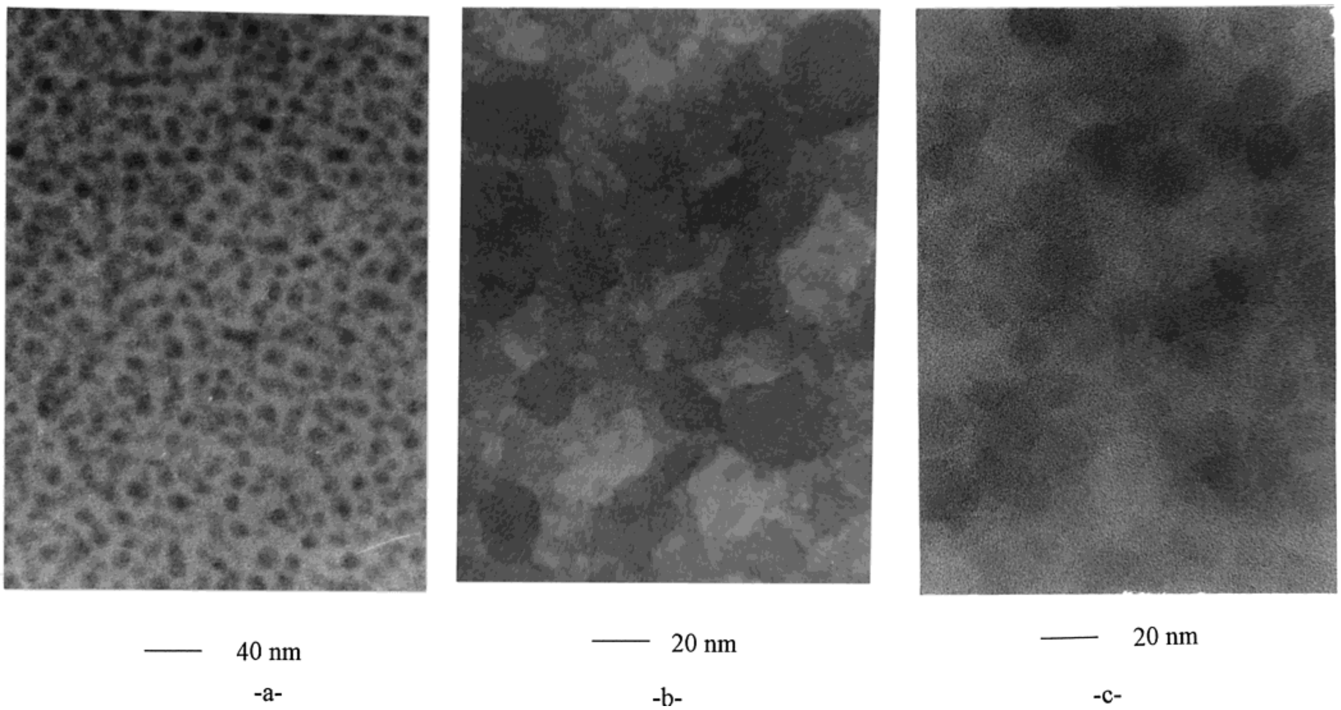

Figure 2. TEM photographs: (a) POM_1-containing solution ($[POM_1]_0 = 4.2 \times 10^{-2}$ mol·L^{-1}, $[AAm]_0 = 0.84$ mol·L^{-1}, corresponding to the initial conditions for the synthesis of the hydrogel **7**); (b) type I hydrogel, sample **7**; (c) type II hydrogel, sample **20** ($[POM_2]_0 = 1.2 \times 10^{-2}$ mol·L^{-1}, $[BAAm]_0 = 1.7 \times 10^{-2}$ mol·L^{-1}, $[AAm]_0 = 0.84$ mol·L^{-1}).

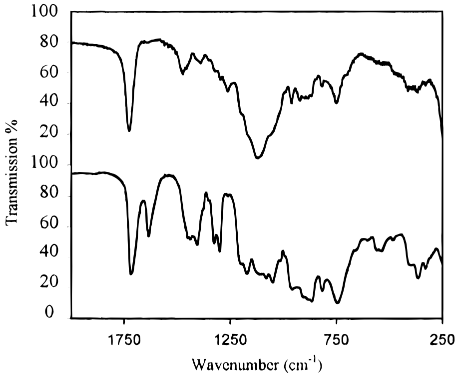

Figure 3. IR spectra of the sample obtained from the reaction of the polyanions POM_1 in the presence of the hydrosoluble initiator and in the absence of acrylamide (top) and of the starting solution (bottom).

To obtain information on the eventual covalent structure of the aggregates, POM_1 was polymerized at 70 °C in the sole presence of the water-soluble initiator $K_2S_2O_8$. As the polymerization proceeded, a very brittle gel was formed, which was found to correspond to polyanions without residual double bonds (Figure 3). Consequently, if the penetration of the primary radicals arising from the thermal decomposition of the initator in the aggregates is questionable, propagating radicals can be brought from the aqueous phase by an active chain made of a few polymerized free polyanions. To illustrate this assumption, it should be mentioned that, in the case of sodium dodecyl sulfate micelles, 10^3-10^5 exchanges with the aqueous continuum may occur per second.[9] This frequency is very probably lower in the case of the polyoxotungstates due to their high molecular weight (3195) and therefore to their reduced mobility, but it is expected that a very high number of exchanges are possible during the lifetime of the propagating species.

Swelling Properties of Type I Gels. For the first set (gels 1−5, Table 1), the degree of swelling increases considerably when the initial monomer and cross-linker concentrations decrease, while the $[\text{monomer}]_0/[\text{cross-linker}]_0$ ratio is almost constant. It would appear that the degrees of swelling of gels **4** and **5** (196 and 268 g/g, respectively) are in the bottom range of those of superabsorbent materials (typically, $(m - m_0/m_0) = 100-1000$ g/g).

The second set (gels **3** and **6**−**8**, Table 1) shows that the water regain decreases considerably when increasing the molar fraction of the polyanion increases. Those results cannot be discussed without preliminary remarks. On one hand, the polyanion may act as a tetrafunctional molecular cross-linker; on the other, the aggregation of N polyanions leads to nano-cross-linkers whose nominal functionality is $4N$. From this point of view, the reaction mixture initially contains two cross-linking species whose effective concentrations and average functionality depend on the aggregation equilibrium constant. In addition, the polyanions are charged species which behave as polyelectrolytes whatever their aggregation state.

Characterization and Swelling Properties of Type II Gels. To gain insight into the cross-linker *versus* polyelectrolyte effect, the swelling properties of classical *N,N*′-methylenebis(acrylamide) cross-linked polyacrylamide hydrogels were compared to those of type II hydrogels (Table 2, gels **9**−**15** and **16**−**22**, respectively).

Type II hydrogels contain trapped POM_2 spherical aggregates (Figure 2c). Figure 4 (curves 2 and 3) shows that the degree of swelling at equilibrium is higher when polyanions are trapped inside the gel. This result is in agreement with those obtained by Philipova *et al.* for polyacrylamide hydrogels with embedded rodlike polyelectrolytes.[7] These authors have ascribed the gel swelling to the osmotic pressure exerted by the coun-

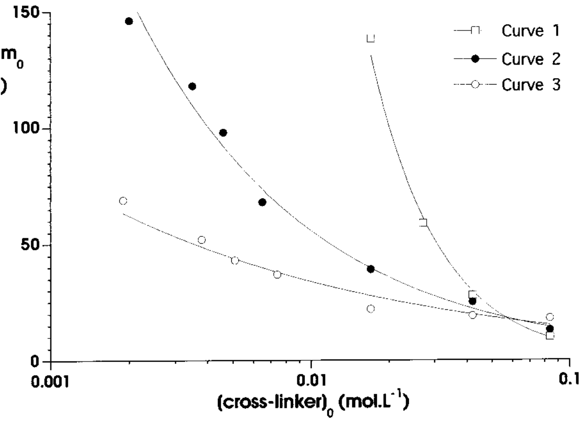

Figure 4. Degree of swelling of the hydrogels as a function of the nominal cross-linker concentration: type I hydrogels (curve 1); type II hydrogels (curve 2), and *N*,*N*′-methylenebis(acrylamide) cross-linked polyacrylamide hydrogels (curve 3).

terions of the stiff-chain polyelectrolyte. This explanation holds for type II hydrogels.

To appreciate the intensity of the effect, gels **23**−**25** were prepared (Table 2). The $[BAAm]_0/[AAm]_0$ ratio was kept constant for three different POM_2 contents. The degree of swelling increases very slightly, while the concentration of POM_2 is increased *ca.* 4 times. The polyelectrolyte effect is weak.

This first part gives information on the contribution of the polyanion aggregates as polyelectrolytes to the gel swelling. When these aggregates are able to copolymerize with acrylamide, they act further as a cross-linking agent.

Cross-Links Ensured by Polyanion Aggregates *versus* Free Polyanions. Whatever the initial concentration of the polyanion, we should consider that, above the CAC, both species are present and participate in the cross-linking.

When the copolymerization of acrylamide and POM_1 was carried out at a concentration of POM_1 just below its CAC ($[POM_1]_0 = 4 \times 10^{-4}$ mol·L^{-1}), the formation of a gel was observed; its swelling degree at equilibrium was 150 g/g. Above the CAC, an increase of the initial POM_1 concentration gives rise to an increase of the polyanion aggregates, whereas the concentration of the free polyanions remains almost constant.

In Figure 4, curve 1 shows that the degree of swelling of type I hydrogels considerably decreases when the nominal polyanion concentration increases. Furthemore, the degree of swelling is decreased *ca.* 14-fold when the concentration changes by an order of magnitude. This tremendous variation can be ascribed to the presence of aggregates whose effect as multifunctional cross-linkers depends on their concentration and functionality; both are governed by the mean aggregation number *N*.

In Figure 5a are shown the expected variations of the concentrations of aggregates as a function of the total concentration of POM_1 and *N*. The effective concentration of the cross-linkers is the sum of those of the tetrafunctional free polyanions and of the 4*N*-functional aggregates (Figure 5b). This varies strongly in the case of the lowest aggregation numbers.

Therefore, it would appear that the strong variation of the swelling degree with a change of the total polyanion concentration by an order of magnitude (in the range of relatively high concentrations) may be due to a significant increase of the concentration of aggregates having therefore rather low *N* values. Conversely, a phase transition could be responsible for this variation.

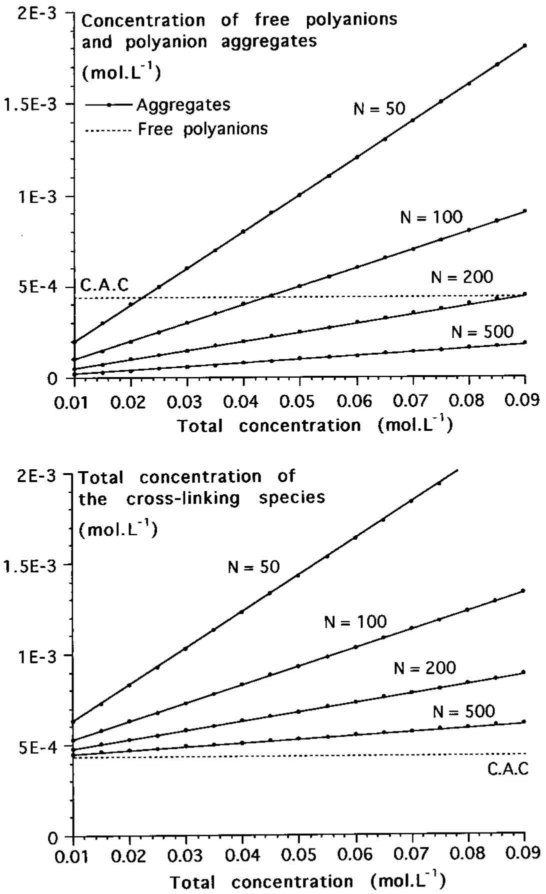

Figure 5. Expected variations of the nominal concentration of the aggregates (a, top) and of the cross-linking species concentrations (b, bottom) as a function of the mean aggregation number *N*.

Conclusion

In this paper we report on the synthesis of networks *covalently* cross-linked by hybrid organic−inorganic clusters. These compounds are surfactants which lead to hydrogels with peculiar swelling properties. In particular, the degrees of swelling of the gels synthesized in the presence of polyanions at $[POM_1]_0 = 4 \times 10^{-4}$ (<CAC) and 1.7×10^{-2} (≫CAC) mol·L^{-1} are similar. This result raises the question of the swelling degree of gels prepared from POM_1 solution at concentrations between 4×10^{-4} and 1.7×10^{-2} mol·L^{-1}. Is the degree of swelling constant over this range of concentration varying by 3 orders of magnitude? In the former case, this would open a new type of hydrogel materials in which the mechanical and intrinsic properties can be adjusted by appropriate amounts of polyoxotungstates without giving rise to a variation of the degree of swelling at equilibrium. In the latter, an original variation of the degree of swelling as a function of the cross-linker concentration would be expected.

On the other hand, these hydrogels have been prepared in the presence of maghemite nanoparticles (γ-Fe_2O_3) coated by citrate species.[10] New magnetic gels were obtained with potential applications in magnetorheology, magnetostriction, and biomaterials. A full report will be published in due course.

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