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## Communications

### New Hybrid Covalent Networks Based on Polyoxometalates: Part 1. Hybrid Networks Based on Poly(ethyl methacrylate) Chains Covalently Cross-linked by Heteropolyanions: Synthesis and Swelling Properties

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Polyoxometalates (POM) have been studied in several disciplines and their applications have been developed on combinations of the so-called value-adding properties.<sup>1,2</sup> Photo- and electrochromism,<sup>3</sup> catalysis,<sup>4</sup> and magnetism<sup>5</sup> are significant examples of the polyanion properties whose transfer in materials has become an attractive field. In a larger extent, several strategies to

design hybrid organic–inorganic materials have been reported by Sanchez et al. in comprehensive reviews.<sup>6–8</sup>

Entrapment in polymeric networks has extensively been studied<sup>2–5,9</sup> but only one article reported on functionalized POM covalently linked to an organic polymeric backbone.<sup>10</sup> Functionalized POM were used as monomers and, according to the author, their radical polymerization led to hybrid polymers with linear or branched and compact structures, depending on the polymerization conditions. If the formation of linear chains is questionable due to the unfavorable head–head additions of the polymerizable double bonds, the branched and compact structure can be regarded as a highly cross-linked material built from POM (vinyl)-, (allyl)-, (methacryl)-, or (styryl)-type monomer units.

A third synthetic route to prepare POM containing polymeric materials consists of cross-linking organic polymer chains by functionalized POM. In principle, it can be achieved either by reaction between preformed macromolecules and a cross-linking agent or by copolymerization of a classical monomer and a cross-linker.<sup>11</sup> The functionalization of POM by polymerizable double bonds has been shown to be effective and well-con-

(6) Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, *18*, 1007.

(7) Sanchez, C.; Ribot, F.; Lebeau, B. *J. Mater. Chem.* **1999**, *9*, 35.

(8) Ribot, F.; Sanchez, E. *Comments Inorg. Chem.* **1999**, *20*, 327.

(9) For relevant pioneering studies, see: (a) Nomiyama, K.; Murasaki, H.; Miwa, M. *Polyhedron* **1986**, *5*, 1031. (b) Shimidzu, T.; Ohtani, A.; Aiba, M.; Honda, K. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3941. (c) Keita, B.; Nadjo, L. *J. Electroanal. Chem.* **1988**, *255*, 303. (d) Keita, B.; Essaadi, K.; Nadjo, L. *J. Electroanal. Chem.* **1989**, *259*, 127. (e) Bidan, G.; Lapowski, M. *Synth. Met.* **1989**, *28*, C113. (f) Keita, B.; Nadjo, L. *Mater. Chem. Phys.* **1989**, *22*, 77. For recent works, see: Klemperer, W. G.; Wall, C. G. *Chem. Rev.* **1998**, *98*, 297.

(10) Judeinstein, P. *Chem. Mater.* **1992**, *4*, 4.

(11) Labana, S. S. *Cross-linking*; Encyclopedia of Polymer Science and Engineering, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; John Wiley & Sons: New York, 1986; Vol. 4, pp 350.

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(1) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.

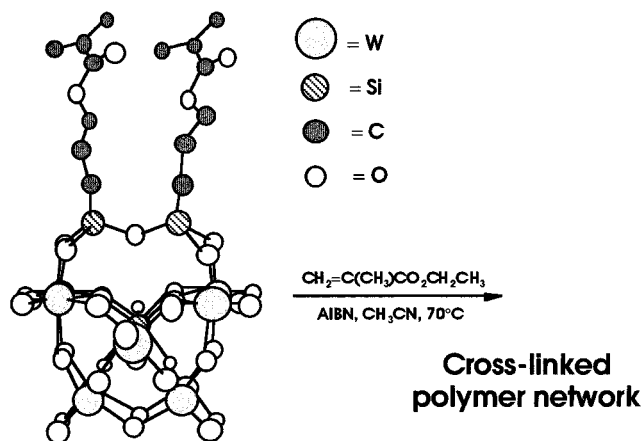
(2) Katsoulis, D. E. *Chem. Rev.* **1998**, *98*, 359.

(3) Yamase, T. *Chem. Rev.* **1998**, *98*, 307.

(4) Sadakane, M.; Steckhan, E. *Chem. Rev.* **1998**, *98*, 219. Mizuno,

N.; Misono, M. *Chem. Rev.* **1998**, *98*, 199.

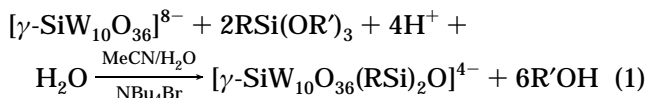
(5) Coronado, E.; Gómez-García, C. J. *Chem. Rev.* **1998**, *98*, 273.



**Figure 1.** Representation of the functionalized polyanion,  $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{HC}=\text{C}(\text{Me})\text{C}(\text{O})\text{OPrSi})_2\text{O}]^{4-}$  copolymerized with ethyl methacrylate in acetonitrile at 70 °C in the presence of 2,2'-azobis(isobutyronitrile) (AIBN) as radical initiator.

trolled,<sup>12</sup> so that the latter option has been retained. This communication reports on the synthesis of hybrid networks made of organic polymer chains covalently cross-linked by heteropolyanions through free radical copolymerization.

**Preparation of the Hybrid Cross-Linkers.** The reaction between the divacant heteropolyanion  $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$  as  $\text{K}^+$  salt and trimethoxysilylpropyl methacrylate allows polymerizable double bonds to be grafted onto the inorganic compound. The functionalized polyoxometalate  $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{HC}=\text{C}(\text{Me})\text{C}(\text{O})\text{OPrSi})_2\text{O}]^{4-}$  ( $\text{POM}_2$ ) has been obtained as  $[\text{NBu}_4]^+$  salt according to



where  $\text{R} = \text{CH}_2=\text{C}(\text{Me})\text{C}(\text{O})\text{OPr}$  and  $\text{R}' = \text{CH}_3$ , and its structure was characterized by  $^{29}\text{Si}$ ,  $^{183}\text{W}$ , and  $^1\text{H}$  NMR, IR spectroscopy, and mass spectrometry (Figure 1).<sup>12</sup>

With the use of a quaternary onium bearing a methacrylate group  $[(\text{Me})_3\text{N}^+\text{C}_2\text{H}_4\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2]$ , polymerizable functionalities can be further introduced on the cationic moiety of the hybrid compound. The trifunctionalized species  $\text{POM}_3$  has thus been obtained from  $\text{POM}_2$ .<sup>13</sup> Unlike the latter, the former has two covalently linked propyl methacrylate substituents along with one more polymerizable function that interacts with the polyanion ionically.

**Synthesis and Characterization of the Gels.** Ethyl methacrylate (EMA) and POM were copolymerized in  $\text{CH}_3\text{CN}$  at 70 °C using 2,2'-azobis(isobutyronitrile) (AIBN) as radical initiator (Figure 1).<sup>14</sup> Sol-gel

transitions were observed at different times depending on both the  $[\text{EMA}]_0/[\text{POM}]_0$  ratio and the functionality of the polyanion.  $\text{CH}_3\text{CN}$  swollen gels were recovered in all experiments (gels **1**, **2**, and **3** for  $[\text{EMA}]_0/[\text{POM}_2]_0 = 10$ , 20, and 50, respectively, and gel **4** for  $[\text{EMA}]_0/[\text{POM}_3]_0 = 50$ ). As these reaction products were introduced in a largest volume of  $\text{CH}_3\text{CN}$ , they did not solubilize, but swelled until the equilibrium (see further: Swelling Properties of the Gels). This observation accounts for the formation of networks.

On the other hand, when the polymerization was carried out in the absence of functionalized POM or in the presence of unfunctionalized POM,<sup>15</sup> no gel was formed, whereas poly(ethyl methacrylate) formation was checked by precipitation of the polymer in methanol.

In Figure 2, the  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_3\text{CN}$  swollen state shows that the vinylic protons of the functionalized polyanion (5.52 and 6.05 ppm for  $\text{POM}_2$ ) as well as those of the monomer (5.57 and 6.07 ppm) are no longer present. The IR analysis of the gel in dry state (Table 1) corroborated the absence of the polymerizable double bonds by the disappearance of the bands at 1636 and 1639  $\text{cm}^{-1}$  ( $\nu_{\text{as}}(\text{C}=\text{C})$  of  $\text{POM}_2$  and ethyl methacrylate). Concurrently, a shift from 1713 and 1715 to 1729  $\text{cm}^{-1}$  ( $\nu_{\text{a}}(\text{C}=\text{O})$  of  $\text{POM}_2$ , ethyl methacrylate and **2**) attests to the loss of conjugation.

The assignments proposed in Figure 2 account for the formation of poly(ethyl methacrylate) chains. In particular, signals **1** and **6** correspond to  $\beta\text{-CH}_2$  of polymerized EMA and of methacrylic units grafted to the heteropolyanion. However,  $\text{CH}_3$  (**2** and **7**) overlay with  $\gamma\text{-CH}_2$  of tetrabutylammonium (**12**) and  $\text{CH}_3$  of the ester function (**9**), which makes the characterization of the polymer microstructure very difficult. The  $[\text{EMA}]_0/[\text{POM}_2]_0$  ratio into the gel can be calculated from signals **3**, **8**, and **10** and is equal to 6, which is a value about three times lower than the composition in the feed ( $[\text{EMA}]_0/[\text{POM}_2]_0 = 20$ ). As usually observed for gel synthesis, the formation of a network does not allow the monomer consumption to be completed. However, no residual double bond has significantly been characterized into the gel in swollen ( $^1\text{H}$  NMR) and dry states (IR); it implies that the unreacted monomer has been eliminated during the preparation of the sample before analysis.

**IR,  $^{29}\text{Si}$  and  $^{183}\text{W}$  NMR Analysis of the Polyoxometallic Moiety in the Gels.** IR data reported in Table 1 shows that the polyanion in the gel (dry state) presents almost the same stretching [ $\nu_{\text{as}}(\text{W}=\text{O}_{\text{ter}})$  and

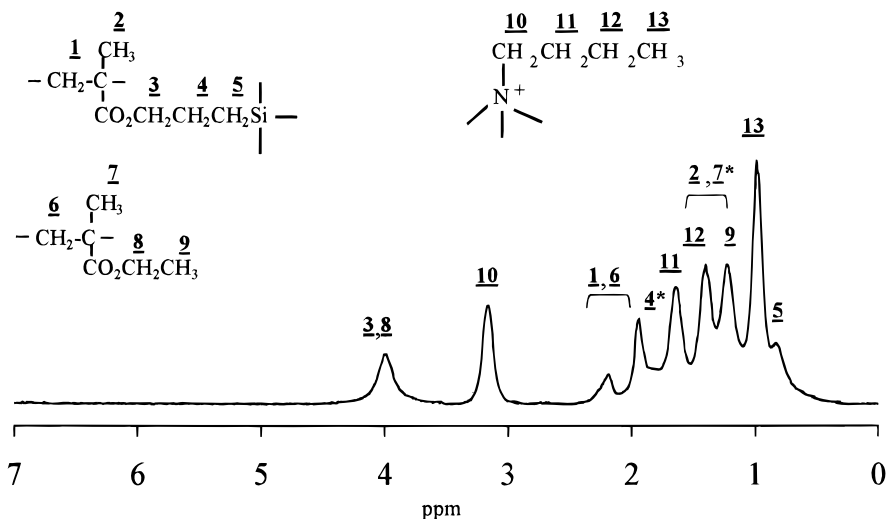
1.93 (s, 6H,  $=\text{C}(\text{CH}_3)-\text{O}^{\text{b}}$ ), 1.90 (s, 3H,  $=\text{C}(\text{CH}_3)-\text{O}^{\text{a}}$ ), 1.78 (q, 4H,  $-\text{CH}_2-\text{O}^{\text{b}}$ ), 1.60 (m, 16H,  $-\text{CH}_2-\text{O}^{\text{c}}$ ), 1.40 (m, 16H,  $-\text{CH}_2-\text{O}^{\text{c}}$ ), 0.98 (t, 24H,  $-\text{CH}_3^{\text{c}}$ ) and 0.64 ppm (t, 4H,  $-\text{CH}_2-\text{Si}^{\text{b}}$ ); a-c superscripts are referred to  $(\text{Me})_3\text{N}^+\text{C}_2\text{H}_4\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$ ,  $[\text{SiW}_{10}\text{O}_{36}(\text{HC}=\text{C}(\text{Me})\text{C}(\text{O})\text{OPrSi})_2\text{O}]$ , and  $[\text{N}(\text{C}_4\text{H}_9)_4]^+$ , respectively. The quantitative analysis confirmed the presence of two covalently linked propyl methacrylate substituents along with one  $(\text{Me})_3\text{N}^+\text{C}_2\text{H}_4\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$  functionality.

(14) A typical procedure for the synthesis of gel **3**: the polyanion (0.8 g, 0.23 mmol) and ethyl methacrylate (1.43 mL, 11.4 mmol) were dissolved in  $\text{CH}_3\text{CN}$  (4.6 mL). The solution was degassed with argon. 2,2'-azobis(isobutyronitrile) (19 mg, 0.114 mmol) was added, and the reaction mixture was heated at 70 °C during 12 h. Then the gel was allowed to swell in  $\text{CH}_3\text{CN}$  (100 mL) until equilibrium. The dry gels were obtained by solvent evaporation at 110 °C. For gels **1**, **2**, and **4**, the same procedure was followed with appropriated amounts of reactants according to the  $[\text{EMA}]_0/[\text{POM}]_0$  ratio.

(15)  $[(n\text{-Bu})_4\text{N}]_3\text{H}[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhSi})_2\text{O}]$  was prepared according to ref 12.

(12) Mayer, C. R.; Fournier, I.; Thouvenot, R. *Chem. Eur. J.* **2000**, 6, 105.

(13)  $\text{POM}_3$  was prepared as follows:  $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}] \cdot 12\text{H}_2\text{O}$  was synthesized according to a previously described procedure (Canny, J.; Tézé, A.; Thouvenot, R.; Hervé, G. *Inorg. Chem.* **1986**, 25, 2114). To the starting polyanion (2.97 g, 1 mmol) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  suspension (30 and 8 mL respectively), were successively added  $\text{NBu}_4\text{Br}$  (0.64 g, 2 mmol),  $\text{H}_2\text{C}=\text{C}(\text{Me})\text{C}(\text{O})\text{OPrSi}(\text{OMe})_3$  (0.47 mL, 2 mmol) and  $\text{Cl}^-(\text{Me})_3\text{N}^+\text{C}_2\text{H}_4\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$  (0.2 mL, 1 mmol). Then 0.5 mL of 12 M HCl was added, and the reaction mixture was vigorously stirred for 6 h. A white compound was formed. It was recovered from the reaction mixture by solvent evaporation then washed with water.  $^1\text{H}$  NMR data in  $\text{CD}_3\text{CN}$  (300 MHz): 6.12 (s, 1H,  $\text{H}_\text{a}=\text{c}$ ), 6.06 (s, 2H,  $\text{H}_\text{a}=\text{b}$ ), 4.6 (m, 2H,  $-\text{C}(\text{O})\text{CH}_2-\text{a}$ ), 4.1 (q, 4H,  $-\text{C}(\text{O})\text{CH}_2-\text{b}$ ), 3.8 (t, 2H,  $-\text{CH}_2-\text{N}-\text{a}$ ), 3.1 (m, 16H,  $-\text{CH}_2-\text{N}-\text{c}$ ), 2.44 (s, 9H,  $-\text{N}-(\text{CH}_3)_3$ ),



**Figure 2.** A 300.13 MHz  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_3\text{CN}$  swollen state (reference: TMS). The asterisk (\*) indicates the  $\gamma\text{-CH}_2\text{-}$  of tetrabutylammonium (**12**) and  $\text{-CH}_3$  of the ester function (**9**) overlay  $\text{-CH}_3$  (**2** and **7**);  $\text{-CH}_2\text{-}$  (**1** and **6**) overlay  $\text{-CH}_2\text{-}$  (**4**).

**Table 1. Most Relevant Infrared Data ( $\text{cm}^{-1}$ ) of Gels **2** and **4** (Dry State)<sup>a</sup>**

assignments	POM <sub>2</sub>	gel <b>2</b>	POM <sub>3</sub>	gel <b>4</b>	monomer
$\nu_{\text{as}}(\text{CO}_2)$	1713 vw	1729 vw	1713 vw	1729 vw	1715 vw
$\nu_{\text{as}}(\text{C}=\text{C})$	1636 s		1635 s		1639 s
$\nu_{\text{as}}(\text{O}-\text{C})$		1177 vw		1176 vw	
		1150 vw		1148 vw	
$\nu_{\text{as}}(\text{Si}-\text{O})^b$	1102 w	1101 m	1103 w	1101 m	
	1058 w	1063 m	1055 w	1063 m	
$\nu_{\text{as}}(\text{C}-\text{O})^c$		1027 m		1027 m	1020 m
$\nu_{\text{as}}(\text{W}=\text{O}_{\text{ter}})$	962 vw	962 vw	965 vw	961 vw	
$\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$	902 vw	902 vw	902 vw	902 vw	
	840 vw	840 vw	868 vw	867 vw	
	821 vw	821 vw	823 vw	821 vw	
	732 vw	732 vw	745 vw	748 vw	
$\delta_{\text{as}}(\text{Si}-\text{O}_b)$	545 s	543 s	545 s	543 s	
	511 s	510 s	511 s	510 s	
$\delta_{\text{as}}(\text{W}-\text{O}-\text{W})$	410 s	410 s	410 s	410 s	
	366 m	366 m	366 m	366 m	

<sup>a</sup> Comparison with those of the di- and trifunctional heteropolyanions (POM<sub>2</sub> and POM<sub>3</sub>, respectively) and of the ethyl methacrylate monomer. The IR spectra ( $4000\text{--}250\text{ cm}^{-1}$ ) were recorded on a Bio-Rad FTS 165 IR FT spectrometer with compounds sampled in KBr pellets. <sup>b</sup> RSiO. <sup>c</sup> Ethyl methacrylate unit.

$\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$  and deformation bands [ $\delta_{\text{as}}(\text{W}-\text{O}_b-\text{W})$ ] characteristic of the  $\gamma$ -isomer than those of the starting functionalized polyanion. This analysis holds for the Si-O vibrations [ $\nu_{\text{as}}(\text{Si}-\text{O})$  and  $\delta_{\text{as}}(\text{Si}-\text{O}_b)$ ] regardless of the functionality of the polyanions.

The  $^{29}\text{Si}$  NMR spectrum of the starting hybrid polyanion (POM<sub>2</sub>) has already been assigned.<sup>12</sup> In summary, it presents two narrow singlets at  $-63.2$  and  $-87.9$  ppm with relative intensities 2:1 (Figure 3a and Table 2). The high-frequency singlet is assigned to the RSi group and the low one to the central  $\text{SiO}_4$  unit of the polyoxotungstate. Two broad resonances ( $-62$  and  $-88$  ppm) are observed in the spectrum of **2** (Figure 3b and Table 2). The position of these two signals at nearly the same chemical shifts confirms the retention of the structure of the starting hybrid polyanion. Moreover, the broadening of these resonances is assigned to the reduced mobility of the POM<sub>2</sub> units in the swollen gel.

The starting polyanion exhibits 2:1:2 pattern in the  $^{183}\text{W}$  NMR spectrum, consistent with  $C_{2v}$  symmetry of the  $\{\gamma\text{-SiW}_{10}\text{O}_{36}\}$  framework (Figure 3c and Table 2).<sup>12</sup> The same pattern and similar chemical shifts are

observed for the gel with a broadening of the signals (Figure 3d and Table 2).

According to these analyses, it would appear that the structural integrity of the polyoxotungstate moiety has been preserved. It is therefore expected that the intrinsic properties of the polyanion engaged in the cross-linking knots should express through the gel.

**Swelling Properties of Gels 1–4.** Swelling can be expressed in weight, volume, and chain length units.<sup>16</sup> In Table 3, it corresponds to the swelling index ( $I_{\text{sw}}$ ) at the swelling equilibrium and was calculated according to

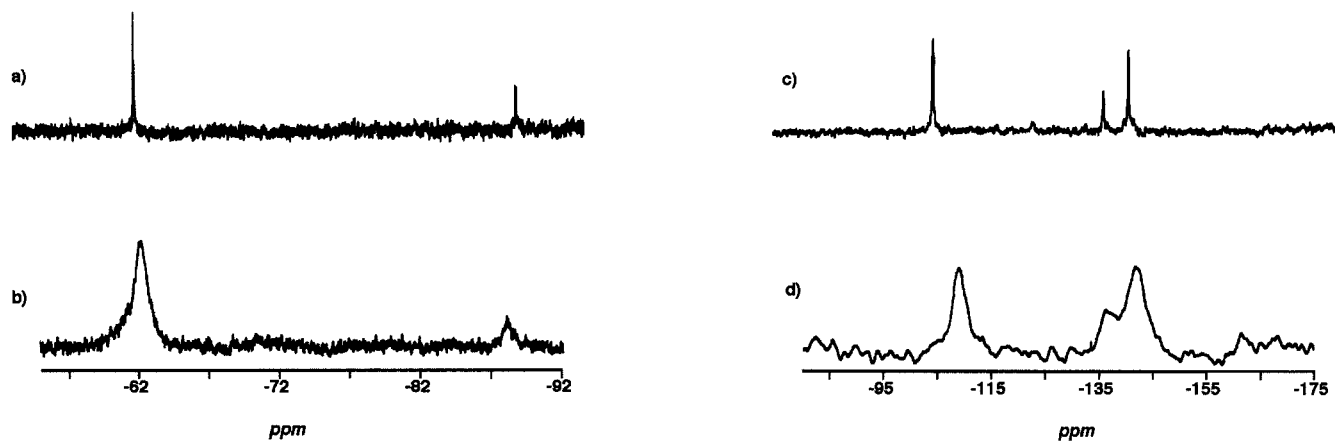
$$I_{\text{sw}} (\text{g/g}) = (\text{wet weight} - \text{dry weight}) / \text{dry weight} \quad (2)$$

It corresponds to the weight of the solvent (wet weight of the gel – dry weight of the gel) that the dry material (dry weight of the gel) is able to absorb. Data reported in Table 3 (entries 1–3) shows that  $I_{\text{sw}}$  increases with increasing the initial  $[\text{EMA}]_0/[\text{POM}_2]_0$  ratio (gels **1–3**). As expected, the extent of gel solvation depends on the cross-linking density which is imposed by the initial  $[\text{EMA}]_0/[\text{POM}_2]_0$  ratio.

The functionality of the cross-linker influences  $I_{\text{sw}}$  values as shown by the comparison of data relative to gels **3** and **4** (entries 3 and 4).  $I_{\text{sw}}$  is decreased by  $\sim 17$  times for gel **4** with respect to gel **3**. Since three poly(ethyl methacrylate) chains (gel **4**) vs two (gel **3**) can be connected to the cross-linking knots, the density of cross-linkages of gel **4** should be higher than that of gel **3**. The well-known effect of the functionality of the cross-linker on swelling properties is particularly marked here. This behavior is an interesting feature because the third functionality of POM<sub>3</sub> is brought by a ionically interacting methacrylic substituent.

The influence of the solvent nature is shown in Table 3 (entries 2 and 5–9). Two sets of solvents have been tested according to the respective solubilities of POM and poly(ethyl methacrylate). The highest  $I_{\text{sw}}$  values are obtained when both the cross-linker and the polymer are soluble (entries 2, 5, and 6). Interestingly, in

(16) Kudela, V. *Hydrogels*; Encyclopedia of Polymer Science and Engineering, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; John Wiley & Sons: New York, 1987; Vol. 7, pp 783.



**Figure 3.** For a and b respectively, 99 MHz  $^{29}\text{Si}$  NMR spectra of the starting difunctional polyanion and of the corresponding gel **2** in swollen state ( $[\text{EMA}]_0/[\text{POM}_2 \text{ or } 3]_0 = 20$ ). Conditions of  $^{29}\text{Si}$  NMR measurements: Bruker AM 500 spectrometer; 10 mm o.d. tubes; nearly saturated solutions in DMF-( $\text{CD}_3$ ) $_2$ CO mixture (90/10 v/v); 300 K; pulse angle  $90^\circ$ ; acquisition time 0.82 s for a and 2.05 s for b; 3 200 scans for a and 33 000 for b. For c and d respectively, 12.5 MHz  $^{183}\text{W}$  NMR spectra of the same compounds. Conditions of  $^{183}\text{W}$  NMR measurements: Bruker AC 300 spectrometer equipped with a low-frequency special VSP probehead; 10 mm o.d. tubes; nearly saturated solutions in DMF-( $\text{CD}_3$ ) $_2$ CO mixture (90/10 v/v); 300 K; pulse angle  $90^\circ$ ; acquisition time 1.37 s; 16 200 scans for c and 68 000 for d.

**Table 2.**  $^{29}\text{Si}$  and  $^{183}\text{W}$  NMR Data of Gel **2**<sup>a</sup> and Comparison with Those of the Difunctional Heteropolyanion  $\text{POM}_2$ <sup>b</sup>

sample	$\delta$ (ppm)				
	$^{29}\text{Si}$ NMR		$^{183}\text{W}$ NMR		
$\text{POM}_2$	-63.2	-87.9	-107.3	-135.9	-140.3
<b>2</b>	-62	-88	-107	-136	-140

<sup>a</sup> The 99.4 MHz  $^{29}\text{Si}$  and 12.5 MHz  $^{183}\text{W}$  NMR spectra were recorded at 300 K on a nearly saturated DMF-( $\text{CD}_3$ ) $_2$ CO (90/10 v/v) solution. <sup>b</sup> Same conditions for the NMR analysis of gel; the gel was swollen in a nearly saturated DMF-( $\text{CD}_3$ ) $_2$ CO (90/10 v/v) mixture.

solvents that solubilize poly(ethyl methacrylate) chains only (entries 7–9), the gel is solvated very poorly. This observation accounts for a substantial contribution of the heteropolyanion to the swelling properties of the gel. Although the molar concentration of the heteropolyanion is low with respect to that of the monomer, its weight fraction into the gel is high. Thus, when it is insoluble, less solvent can be regained by the gel and the solvation percentage falls.

**Conclusions.** The copolymerization of EMA and functionalized polyanions led to the formation of networks. Several key points have been investigated such as the efficiency of the polyanions as cross-linkers, the retention of their structural integrity and their contribution to the swelling properties of the gels. This study

**Table 3.** Swelling Index ( $I_{\text{sw}}$ )<sup>a</sup> of Gels 1–4 at Swelling Equilibrium and at 25 °C as a Function of the Monomer/Cross-Linker Composition in the Feed ( $[\text{EMA}]_0/[\text{POM}]_0$ ),<sup>b</sup> of the Functionality of the Heteropolyanion ( $f$ )<sup>c</sup> and of the Nature of the Solvent

entry	gel	$[\text{EMA}]_0/[\text{POM}_2 \text{ or } 3]_0$	solvent	$I_{\text{sw}}$ (g/g) <sup>d</sup>
1	1	10	$\text{CH}_3\text{CN}$	9.6
2	2	20	$\text{CH}_3\text{CN}$	29.9
3	3	50	$\text{CH}_3\text{CN}$	58.4
4	4	50	$\text{CH}_3\text{CN}$	3.5
5	2	20	DMF	23.1
6	2	20	DMSO	22.6
7	2	20	$\text{CH}_2\text{Cl}_2$	5.5
8	2	20	$\text{CHCl}_3$	4.8
9	2	20	toluene	1.2

<sup>a</sup> The swelling index is defined according to eq 2. <sup>b</sup> Mole ratio. <sup>c</sup>  $f = 2$  for all gels except for gel **4** ( $f = 3$ ). <sup>d</sup>  $I_{\text{sw}}$  is expressed in g/g, namely, grams of solvent per grams of dry gel.

will be extended to the synthesis of new hybrid networks based on hydrosoluble polymer chains covalently cross-linked by heteropolyanions.<sup>17</sup>

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(17) Mayer, C. R.; Thouvenot, R.; Lalot, T. Submitted to *Macromolecules*.