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[8] Preparation of **5**: In a thick-walled 5-mL screw-cap flask, $Pd(OAc)_2$ (11.2 mg, 50 μmol, 5 mol%), PPh_3 (26.2 mg, 100 μmol, 10 mol%), bicyclopropylidene (**1**) (160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.0 mmol), and 1,4-diiodobenzene (166 mg, 0.500 mmol) were stirred with methyl acrylate (**3a**) (288 mg, 3.35 mmol) in anhydrous DMF (1 mL) for 48 h at 80°C under argon. After the addition of Et_2O (15 mL), washing with H_2O (3×10 mL), drying over $MgSO_4$, and removal of the solvent, the residue was purified by column chromatography (column 2×20 cm, pentane/Et_2O (2/1)), and **5** (130 mg, 64%) was obtained as colorless crystals, $R_f = 0.32$ (Et_2O). IR (film): $\tilde{\nu} = 3078, 3047, 2927, 1734$ (C=O), 1653 cm^{-1} (C=C); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.68-0.72$ (m, 2H, cyclopropyl-H), 0.75 (m_c, 2H, cyclopropyl-H), 0.81 (m_c, 2H, cyclopropyl-H), 0.90 (m_c, 2H, cyclopropyl-H), 1.77 (dd, $^2J = 13.0$, $^3J = 3.5$ Hz, 2H, 4′-H), 2.47 (dd, $^2J = 13.0$, $^3J = 11.0$ Hz, 2H, 4′-H), 2.76 (dd, $^3J = 9.0$, $^3J = 4.0$ Hz, 4H, 6′-H), 3.18 (ddd, $^3J = 11.0$, $^3J = 9.0$, $^3J = 3.5$ Hz, 2H, 5′-H), 3.98 (s, 6H, OCH_3), 5.80 (t, $^3J = 4.0$ Hz, 2H, 7′-H), 7.08 (s, 4H, Ar-H); ^{13}C NMR (125.7 MHz, $CDCl_3$, APT): $\delta = 11.59$ (–, cyclopropyl-C), 12.91 (–, cyclopropyl-C), 20.09 (–, C-3′), 28.49 (–, C-4′), 37.48 (–, C-6′), 39.38 (+, C-5′), 51.64 (+, OCH_3), 123.80 (+, C-7′), 128.25 (+, Ar-C), 138.49 (–, C-8′*), 142.74 (–, Ar-C*), 175.98 (–, CO); MS (70 eV): m/z (%): 406 (31) [M^+], 183 (100) [$M^+ - 2CO - 2MeOH - C_8H_8$], 152 (6), 108 (14), 84 (14), 77 (6); elemental analysis (%): calcd. for $C_{26}H_{30}O_4$ (406.5): C 76.82, H 7.44; found: C 76.65, H 7.43.

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[10] Crystal structure analysis of **5** ($C_{26}H_{30}O_4$): $Z = 4$, $M_r = 406.52$, crystal dimensions: $0.6 \times 0.5 \times 0.3$ mm, monoclinic, space group P-2(1), $a = 629.17(2)$, $b = 1069.44(3)$, $c = 1580.34(4)$ pm, $\beta = 91.311(2)°$, $V = 1.06307(5)$ nm^3, $\rho_{calcd} = 1.270$ $Mg\,m^{-3}$, $F(000) = 436$, $\lambda = 71.073$ pm, $T = 133(2)$ K, $\mu(Mo_{K\alpha}) = 0.084$ mm^{-1}. $2.30 \leq 2\theta \leq 25.03°$; of the 18493 collected reflections, 1882 are independent and were used for the structure refinement of 186 parameters with the help of 105 restraints. The R values are $R1 = 0.0804$ ($I > 2\sigma(I)$) and $wR2 = 0.1281$ (all data); min./max. residual electron density $-236/218$ $e\,nm^{-3}$. The data were collected on a Stoe-Siemens-Huber four-circle diffractometer with a Siemens-CCD surface detector. The intensities were recorded with ϕ and ω scans. The integration of the data was carried out with the programme SAINT. The structure was solved with direct methods (G. M. Sheldrick, SHELXL-93/97, program for crystal structure refinement, Göttingen University, **1997**) and refined against F^2 using the least-squares method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically ideal positions and included in the refinement. All disorders were resolved and refined anisotropically with the help of space and ADP restraints. Crystallographic data (excluding structure factors) of the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133154 (**4f**) and CCDC-133155 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Incorporation of Magnetic Nanoparticles in New Hybrid Networks Based on Heteropolyanions and Polyacrylamide[**]

Cédric R. Mayer, Valérie Cabuil,* Thierry Lalot, and René Thouvenot

Hybrid organic–inorganic materials have received increasing attention over the last few years[1] as a result of the specific properties. This is due to a synergy between both organic and inorganic parts. Functionalized polyanions are good candidates for the elaboration of such materials.[2]

Herein we present a magnetic hybrid hydrogel that results from the incorporation of a magnetic particle from an aqueous dispersion into a polymeric network cross-linked by an organometallic species. The cross-linker is a new water-soluble molecular precursor in the form of a tetrafunctionalized polyoxometalate (POM) of formula $[\gamma\text{-SiW}_{10}O_{36}(RSiO)_4]^{4-}$ ($R = C_3H_6OC(O)C(Me)\!=\!CH_2$).[3] This hybrid consists of a divacant polyanion $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ unit, in

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which a cyclic tetrasiloxane $(RSiO)_4$ is grafted onto the polyoxometalate surface through four Si-O-W bridges (Figure 1).

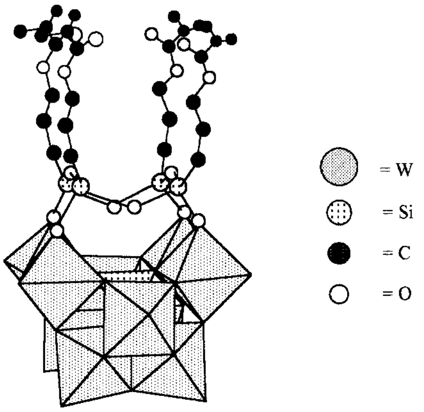

Figure 1. Polyhedral representation of the functionalized polyanion $[\gamma\text{-SiW}_{10}O_{36}(RSiO)_4]^{4-}$ ($R = C_3H_6OC(O)C(Me){=}CH_2$).

This polyanion behaves as a surfactant in water: its surface tension is 43.5 mN m^{-1}, its critical aggregation concentration (CAC) in water is 4.32×10^{-4} M, and the surface area (σ) of its polar head is estimated to be 140 Å^2. It also acts as a cross-linker towards monomers such as acrylamide, and allows the production of gels by usual radical copolymerization. The potassium persulfate initiator is thermally activated in the reaction mixture (see Experimental Section). The propagating polyacrylamide chains are cross-linked by the polyanions during the polymerization and a hybrid network is obtained. The amount of POM in the polymerization mixture controls the density of reticulation. The concentration of the functionalized polyanion in the syntheses is higher than the CAC; thus it forms aggregates in the aqueous polymerization mixture. Analysis by transmission electron microscopy (Figure 2a) confirms the presence of polyanionic aggregates inside the gel. We investigated the effect of three POM/monomer molar ratios (2, 5, and 10%), denoted 2%POM, 5%POM, and 10%POM. Since the polyanionic aggregates are negatively charged, the networks have the ability to be superabsorbent materials. This polyelectrolyte effect[4, 5] allows a swelling ratio (defined as being the ratio m/m_0, where m is the mass of the gel sample swollen in aqueous solution and m_0 the mass of the dry gel) as high as 137.5 for 2%POM gels.

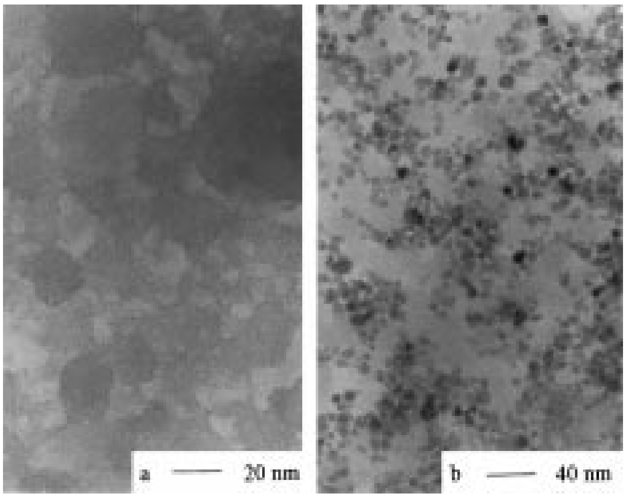

Figure 2. Transmission electron micrographs of the hybrid materials. a) View of a 5%POM gel without magnetic nanoparticles; b) view of the same gel containing maghemite nanoparticles of diameter 7.5 nm (1.4 vol% γ-Fe$_2$O$_3$ particles).

In addition to the potential properties of these new materials such as electrochromism, photochromism, conductivity, electrochemistry, or catalysis, these hybrid materials behave as promising superabsorbents. Unlike polyelectrolytes, the electric charges are located on the polyanionic cross-linkers, and it is possible to incorporate hydrophilic nano-objects with electrostatic charges inside the swelled network. Here we introduce negatively charged magnetic nanoparticles and take advantage of the magnetic properties of the particles to test the characteristics of the network. Some other ferrogels were produced a few years ago for applications in the field of magnetorheology[6] and magnetostriction.[7] These new hybrid hydroferrogels are expected to have applications, for example, in the areas of biomaterials and optics.

The magnetic particles are made of maghemite (γ-Fe$_2$O$_3$). They are polydisperse with an average diameter that can be controlled of between 6 and 14 nm.[8] They are coated by citrate molecules so that they are negatively charged at pH values higher than 4, and can be thus dispersed at pH 7 in water as individual grains as a consequence of electrostatic repulsions. To maintain this stability during the copolymerization process, the polyanions used are obtained at pH 5.4. The copolymerization of acrylamide and the polyanion cross-linker is performed in the dispersion of magnetic particles for different volume fractions of particles. In this way, it is possible to trap large amounts of particles.

Figure 3 shows the magnetization curve of a ferrogel cross-linked by a polyanion (2%POM) with as much as 18 vol% magnetic oxide. It has the same shape as the magnetization curve of the corresponding aqueous dispersion of particles (characteristic of superparamagnetic behavior),[9] which indicates that particles in the gel remain well dispersed. On the other hand, the presence of particles does not seem to modify the structure of the gel. Indeed, the IR spectrum presents the same bands with the same ratio of intensity as a hydrogel formed from the same ratio of reagents but without particles. In the region where the $\nu_{asym}(C{=}O)$ stretching vibrational bands (1600–1730 cm^{-1}) occur, one can observe a shift of the

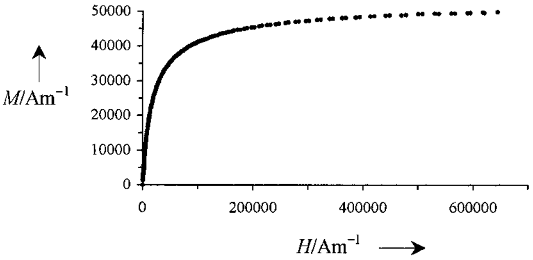

Figure 3. Magnetization curve of a 2%POM ferrogel (18% vol% γ-Fe$_2$O$_3$ particles).

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bands arising from POM from 1713 to 1725 cm^{-1}, and the presence of two bands at 1615 and 1670 cm^{-1} characteristic of polyacrylamide, which attest to the loss of conjugation. The large band at 1119 cm^{-1} supports the formation of polyacrylamide chains. Moreover, the conservation of the polyanionic framework is confirmed by the presence of the same stretching vibrational bands (ν_{asym}(W=O$_{ter}$) and ν_{asym}(W–O$_b$–W)) as those of the polyanion before polymerization.[3] On the other hand, the stretching vibrational bands at 627 and 561 cm^{-1} (ν(FeO)) of maghemite particles are apparent.[10] Figure 2b shows the transmission electron micrograph of a 5 % POM gel, which contains 1.4 vol % maghemite particles (approximately 7.5 nm in diameter). This picture confirms the presence of polyanionic aggregates inside the gel and the presence of γ-Fe$_2$O$_3$ particles between the aggregates.

Figure 4 shows a ferrogel after the synthesis and the same ferrogel swelled in an aqueous solution for four days, which corresponds to the equilibrium degree of swelling. The polyelectrolyte effect of the polyanionic aggregates stays efficient in the ferrogels. It is controlled by the amount of POM, and not by the number of particles in the network. When the amount of POM is increased, the mesh of the polymeric network becomes smaller and the degree of swelling decreases. For example, for a ferrogel with 1.4 vol % particles, the degree of swelling drops from 60-fold for a 2 % POM gel, to 24-fold for a 5 % POM gel, and to 9-fold for a 10 % POM gel.

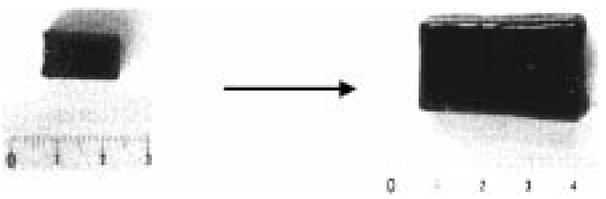

Figure 4. A hybrid 2 % POM ferrogel a) after synthesis; b) swelled in an aqueous solution during four days (5.5 vol % γ-Fe$_2$O$_3$ particles).

The mobility of the nanoparticles in the network can be estimated by taking advantage of their magnetic properties. When a magnetic field is applied to a dispersion of maghemite nanoparticles this dispersion becomes birefringent as a result of the alignment of the particles in the field direction.[11] The value of the birefringence, which reflects the number of particles aligned, allows the estimation of whether particles are immobilized or not in the network. When the field is cut off the birefringence vanishes as these unblocked particles return to random positions at a characteristic rate that is a function of the particle size and of the local viscosity around them (Figure 5). In the case of 8-nm particles (polydisperse system), 5 % POM gels are able to block more particles than 2 % POM gels, and at the same time, the relaxation time is smaller in the first case, which indicates that the unblocked particles are smaller than in the second gel. Since the system is polydisperse, these results lead to the conclusion that the colloidal particles can be either immobilized in the network, or free to rotate, depending on their size and the amount of POM used as cross-linking agent.

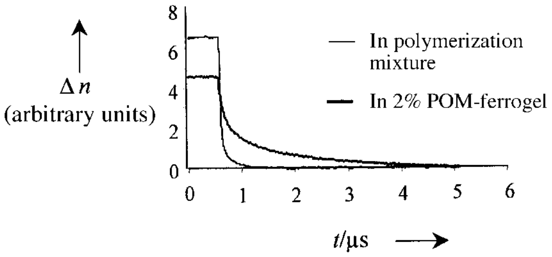

Figure 5. Relaxation of the birefringence signal for the polymerization mixture and for the corresponding ferrogel (molar fraction of POM (0.017 M) with respect to acrylamide (0.84 M): 0.02; 0.25 vol % γ-Fe$_2$O$_3$ particles).

This result is also related to the fact that, depending on the size of the particles, a release of particles during the swelling of the hydrogel can be observed. For example, when monosized particles are introduced into 2 % POM gels, no particles are released if the particle diameter is larger than 9 nm; only 1 % of the magnetic materials is released for 7.5-nm particles and about 5 % is released for 6.1-nm particles. Results of this type have been reported for polymeric gels containing homopolymers of varying mass.[12]

We have presented a hybrid absorbent material based on polyanions covalently linked to a polymeric network with included magnetic nano-sized objects. Two properties are particularly worthy of mention and are important for future applications: the rotational mobility of the particles in the network and their release during the swelling process. For both properties, the relevant parameters are the volume of the mesh of the network, and therefore the ratio of cross-linker, and the diameter of the particles. Indeed, for a given gel at a given degree of swelling, a critical diameter can be defined over which all particles are trapped in the gel. Likewise, this hybrid material is potentially promising for the sorting of nanometric objects on the basis of size. Two areas of application expected for these materials are biomaterials and optics.

Experimental Section

Sample preparation: Magnetite nanoparticles were synthesized according to Massart's method.[13] The mean diameter of the particles was controlled by the experimental conditions used.[14, 15] They were further oxidized to maghemite and then coated by citrate molecules according to reference [8]. Then they were dispersed in water. The ionic strength arose from unadsorbed trisodium citrate and was deduced from conductivity measurements and adjusted to a given value by dialysis of the colloidal solution against a reservoir containing a 8×10^{-3} M solution of trisodium citrate.

[γ-SiW$_{10}$O$_{36}$(RSiO)$_4$]$^{4-}$ (R = C$_3$H$_6$OC(O)C(Me)=CH$_2$) was synthesized following the procedure already described:[3] H$_2$C=C(Me)C(O)O-(C$_3$H$_6$)Si(OMe)$_3$ (0.94 mL, 4 mmol) was added to a solution of K$_8$[γ-SiW$_{10}$O$_{36}$] $\cdot$ 12 H$_2$O[16] (3 g, 1 mmol) in a mixture of CH$_3$CN (30 mL) and H$_2$O (20 mL). The mixture was then acidified with 12 M HCl (0.4 mL) and the solution stirred for 4 h. The hygroscopic crude compound (ca. 3 g) was obtained after evaporation of the mixed solution. The product was then dissolved in deionized water and the pH of the solution raised to 5.4 by an aqueous solution of NaOH. The product was obtained after evaporation of the solution and washing with EtOH (30 mL) and acetone (20 mL), followed by drying under vacuum, and was kept under argon; yield 2.9 g (90.7 %). Elemental analysis (%) calcd for C$_{28}$H$_{45.1}$Na$_{2.9}$Si$_5$W$_{10}$O$_{48}$ (3195.0): C 10.52, H 1.43, Na 2.09, Si 4.39, W 57.54; found: C 11.04, H 1.48, Na 2.07, Si 4.42, W 57.88. IR (KBr): $\tilde{\nu}$ = 1714 cm^{-1} (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) from {$RSiO_3$}), 1081 (vs, ν(SiO) from {$RSiO_3$}), 1058 (vs, ν(SiO) from {$RSiO_3$}), 989 (vw, ν(SiO) from {SiO_4}), 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 POM-ferrogels were prepared by the radical copolymerization of acrylamide (0.84 M) in an aqueous dispersion (pH 7) of γ-Fe_2O_3 particles (volume fraction of particles: 0.25, 0.7, 1.4, 2.75, 7, 12, 18 %), POM (0.017, 0.042, and 0.084 M) as the cross-linker, and potassium peroxodisulfate (2.2×10^{-3} M) as the radical initiator. The polymerization mixture was then heated at 70 °C for 1 h. IR data for a POM ferrogel with [POM] = 0.042 M and a volume fraction of γ-Fe_2O_3 of 11 %, IR (KBr): $\tilde{\nu} = 1725\ \text{cm}^{-1}$ (m, $\nu(CO_2)$ from {RSiO}), 1670 (s, ν(CO) from polyacrylamide), 1615 (m, δ(NH)), 1456 (w, $\delta(CH_2)$), 1414 (w, δ(CH)), 1349 (vw, ν(CN)), 1322 (vw, δ(CH)), 1298 (vw, $\delta(C{-}O{-}CH_2)$ from {RSiO}), 1196 (w, δ(CO)), 1119 (m, $\nu(C{-}C{=}O)$ from {RSiO}), 1053 (w, ν(SiO)), 962 (w, $\nu(WO^{ter})$), 926 (w, ν(WO)), 902 (w, ν(WO)), 866 (w, ν(WO)), 820 (w, ν(WO)), 749 (w, ν(WO)), 627 (vs, ν(FeO)), 561 (vs, ν(FeO)).

Physical measurements: The compound γ-$K_8[SiW_{10}O_{36}] \cdot 8\,H_2O$ was prepared according to the literature.[16] Other reagents, $RSi(OMe)_3$, and solvents were purchased from Aldrich and used as received. Elemental analyses were performed by the Service Central de Microanalyses du CNRS, Vernaison, France. The IR spectra (4000–250 cm^{-1}; KBr) of the compounds and dried hydroferrogels were recorded on a Bio-Rad FTS 165 FT-IR spectrometer. The magnetic measurements were performed by using a classical Foner device.[17] They allow the volume fraction of magnetic particles to be deduced from the saturation magnetization, and the particles size from the shape of the magnetization curve.[9] The apparatus used for the birefringence experiment is described elsewhere.[9] Visualization of POM aggregates and of magnetic particles in the hydroferrogels were performed with a transmission electron microscope (JEOL 100 CX2) on microcoats of hydroferrogel deposited on a carbon-coated copper grid after microtomy at the Centre Régional de Mesures Physiques, Paris. The pictures of the gels were obtained with acharge-coupled device (CDD) color camera (Vista, VPC 4130, UK). Surface tension measurements were obtained at 25 °C on a Krun KT10 tensiometer.

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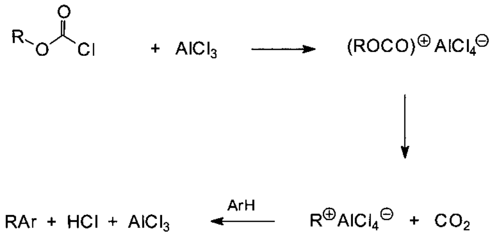
Friedel–Crafts Alkylation of Alkenes: Ethylaluminum Sesquichloride Induced Alkylations with Alkyl Chloroformates**

Ursula Biermann and Jürgen O. Metzger*

Dedicated to Professor Hansjörg Sinn
on the occasion of his 70th birthday

The alkylation of alkenes is of considerable importance.[1] Our interest lies in the alkylation of long-chain unsaturated fatty compounds such as oleic acid (**1a**) since they are renewable raw materials of increasing significance[2, 3] and alkyl-branched fatty compounds have interesting properties.[4] However, there are no methods for the direct alkylation of nonactivated C=C double bonds with simple alkyl residues such as the isopropyl group. Thermal radical addition of alkanes is applicable to terminal double bonds only, not to internal double bonds.[5] Friedel–Crafts alkylations of alkenes, which have been thoroughly investigated by Mayr et al., lead to 1:1 adducts only under certain restricted conditions.[6–9] Thus, $ZnCl_2$-induced reactions of isopropyl chloride with propene or isobutene gave no monoalkylation products, but exclusively oligomers.[6] Cationic additions of alkanes are restricted to tertiary alkanes, for example the formation of isooctane by the reaction of isobutene and isobutane in the presence of concentrated acids.[1, 10]

Friedel and Crafts[11] as well as Rennie[12] showed that benzene is ethylated with ethyl chloroformate in the presence of $AlCl_3$ (Scheme 1).[13] Chloroformates fragment in the presence of Lewis acids with the formation of carbenium



Scheme 1. Friedel–Crafts alkylation of arenes by $AlCl_3$-induced formation of carbenium ions from chloroformates.[13] Ar = Aryl, R = Alkyl.

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