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Hybrid Hydrogels: Macromolecular Assemblies through Inorganic Cross-Linkers

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Summary: The adsorption process onto a silica surface of oligomers from three different monomers, *N,N*-dimethylacrylamide (DMA), *N*-isopropylacrylamide (NIPA) and ethylene oxide (EO), was studied. From the adsorption isotherms and calorimetric experiments, it was shown that *N*-alkylacrylamide derivatives strongly interact with silica nanoparticles. At low coverage ($\Gamma < 0.5\ \mathrm{mg\ m^{-2}}$), the polymers were adsorbed in a flat conformation with a high proportion of trains, while for higher coverages ($\Gamma = 0.5 - 1\ \mathrm{mg\ m^{-2}}$), the adsorption of new chains proceeded by chain displacement, forming an increasing proportion of loops and tails. Similarly, PEO chains readily interacted with silica nanoparticles but showed a lower affinity with an adsorbed amount ($\Gamma \cong 0.6\ \mathrm{mg\ m^{-2}}$) that was approximately half of the value obtained for both PDMA and PNIPA. When these oligomers were grafted onto a non-adsorbing poly(acrylamide-*co*-sodium acrylate) backbone (PAMH), the binding process of these adsorbing side-chains with silica nanoparticles proceeded very similarly and gave rise to the formation of hybrid hydrogels above critical copolymer and silica concentrations. The viscoelastic properties of these networks were controlled by the concentration of inorganic cross-links and the fraction of adsorbing grafts that participated in the formation of bridges between particles, the others being involved in inelastic loops or pendant chains. For all the hybrid mixtures investigated, an optimum weight ratio between silica and grafts was found for the viscoelastic properties, which was in agreement with the saturation of silica beads by the graft precursors. Due to the temperature-dependence of the solubility of the PNIPA side-chains in aqueous solutions, the PAMH-*g*-PNIPA copolymer was also able to self-assemble with temperature, giving rise to a hybrid conetwork in the presence of added silica.

Keywords: hybrid network; hydrogel; poly(*N*-isopropylacrylamide); self-assemblies; silica

Introduction

Aqueous polymer formulations, exhibiting high viscoelastic and self-healing properties at rather low concentrations, find important uses in a wide variety of applications such as pharmaceuticals, cosmetics, paints and enhanced oil recovery.[1,2] In most cases, the formation of transient networks in complex fluids arises from the self-assembling behavior of associating polymers. In water, these associations are generally due to hydrophobic interactions taking place between alkyl, perfluoroalkyl, aromatic or polyacrylate stickers spread out along the water-soluble macromolecules. The synthesis of hydrophobically-modified graft and telechelic architectures, together with their self-assembling properties in semi-dilute aqueous solutions, have been widely reported during the last two decades and have found industrial developments with Hydrophobic Ethoxylated URethane (HEUR) and Hydrophobically-modified Alkali Swellable Emulsions (HASE), for instance.[3–11]

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More recently, the introduction of responsive stickers into the macromolecular architecture has opened up the way of reversible associations and promoted the formation of physical networks under specific environmental conditions. For example, macromolecules designed with polymer sequences characterized by a Lower Critical Solution Temperature (LCST) in water are able to undergo a sol-gel transition in water when increasing the temperature: they are generally called thermoassociating, thermothickening or thermogelling polymers.[12–18] The associating and thermoassociating polymers work on a similar principle: the hydrophobic or responsive stickers self-aggregate into hydrophobic nano-domains that will form temporary junctions between hydrophilic chains. The main difference between these two types of self-assembling polymers arises from the opposite temperature dependence of their associations which render the formulations either thermothickening or thermothinning.[19]

Of course, all the water-based formulations are not simple mixtures of organic compounds and there are numerous situations where inorganic particles are also involved, either as simple additives or as the main component. In these cases, it could be interesting to use or to develop specific interactions between organic and inorganic materials in order to control the viscoelastic properties of complex fluids through hybrid self-assemblies. This was elegantly shown for instance by Haraguchi et al.,[20–21] by polymerizing *N*-alkylacrylamide monomers in suspensions of exfoliated clays. Contrary to chemical hydrogels that are very brittle, nanocomposite hydrogels display superior mechanical properties with a large deformation at break, even at a water content of 90%.

By comparison with these reinforced networks, that are prepared by polymerizing the monomer in a suspension of inorganic particles, we have shown recently[22–24] that hybrid hydrogels can be easily obtained by simply mixing nano-particles in aqueous media with graft copolymers specially designed with adsorbing side-chains (see Figure 1). Furthermore, if the adsorbing grafts display a LCST in water, the temperature or salting out are additional tools that can be used to tune the viscoelastic properties of these hybrid networks. Such a process has been clearly exemplified by mixing silica nanoparticles with poly(acrylamide-*co*-sodium acrylate) (PAMH) grafted either with poly(*N*-isopropylacrylamide) (PNIPA) or poly(propylene oxide) (PPO).[22,23]

In the present paper, our main purpose is to extend the previous concept of hybrid hydrogels to other graft copolymers tailored either with hydrophilic or temperature-responsive side-chains. Following our strategy, various graft copolymers were synthesized using the same non-adsorbing macromolecular backbone (PAMH) and three different adsorbing side-chains: poly(*N,N*-dimethylacrylamide) (PDMA), PNIPA and poly(ethylene oxide) (PEO).[24]

The adsorption behavior of oligomers of DMA, NIPA and EO with silica nanoparticles and the resulting self-assembling properties of the corresponding graft copolymers are reported and compared in the present article.

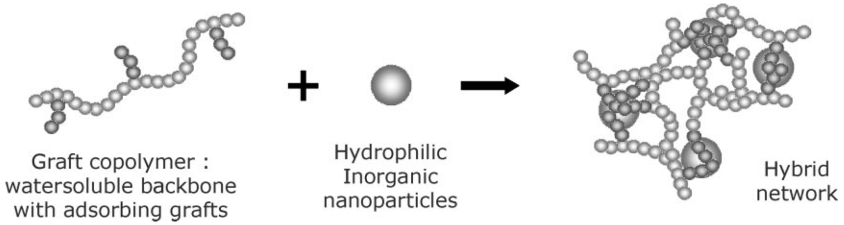


Figure 1.
Schematic representation of hybrid network obtained from self-assemblies between adsorbing grafts and inorganic nanoparticles.

Experimental Part

Nanoparticles

Silica particles (Ludox TM50 from Dupont) were kindly supplied by IMCD France SAS. The crude silica suspension (~50 wt%) was purified by continuous ultrafiltration with water at pH = 8 (membrane cut-off = 10 kDa). Fresh and stable suspensions of negatively charged particles were obtained at concentrations between 25 and 160 g L^{-1} (pH = 8). The characterization of silica particles by small-angle neutron scattering gave a mean radius of $R_0 = 15$ nm with low polydispersity (standard deviation $\sigma = 0.2$ nm). The corresponding specific area was $S_{spe} = 87\,m^2\,g^{-1}$ considering a specific weight $\rho = 2.3\,g\,mL^{-1}$.

Macromolecular Precursors

Jeffamine M-2070, an amino-terminated poly(EO-*co*-PO) with an EO content of 76 mol% and a number-average degree of polymerization $DP_n \cong 37$, was kindly supplied by Huntsman (Belgium). Amino-terminated PDMA and PNIPA were prepared by telomerization, as previously reported[24] using cysteamine hydrochloride as telogen and potassium peroxodisulfate as initiator. PDMA and PNIPA telomers are characterized by a polydispersity index PDI $\cong$ 2 and a $DP_n = 113$ and 75, respectively.

Two PAMH copolymer backbones, containing 70 mol% of acrylamide and 30 mol% of sodium acrylate, were prepared with different molecular weight by radical polymerization of acrylamide followed by partial hydrolysis in alkaline conditions.[24] The two precursors, namely 1-PAMH and 2-PAMH, were characterized by $DP_n = 540$ (PDI = 3.2) and 840 (PDI = 2.4), respectively.

Graft Copolymers[24]

Amino-terminated PDMA, PNIPA or PEO were grafted onto PAMH in aqueous media (pH = 7.3) using a water-soluble carbodiimide as a coupling reagent. The grafting reactions were carried at room temperature for PDMA and PNIPA, and at 60 °C for PEO. As shown by ^1H NMR spectroscopy and size exclusion chromatography performed after the reactions, the grafting yield was almost quantitative. The nomenclature and composition of graft copolymers are given in Table 1.

Table 1.
Nomenclature and composition of graft copolymers.

Copolymer	w_g	n_g	N_g
1-PAMH-*g*-PEO	41	3	16
1-PAMH-*g*-PNIPA	60	1.4	7
2-PAMH-*g*-PDMA	70	1.6	14

w_g: weight percentage of grafts in the copolymer; n_g: average number of grafts per 100 monomer units in the main chain; N_g: average number of grafts per copolymer chain.

Adsorption measurements

Different series of polymer/silica mixtures (pH = 8) were prepared in centrifuge vials by introducing increasing amounts of oligomer (PDMA, PNIPA or PEO) into a silica suspension of fixed concentration ($C_{Si} = 5\,g\,L^{-1}$). The samples were stored under gentle stirring during 72 hours and the silica material was settled down by centrifugation at 25000 g during 12 hours at T = 20 °C. The supernatant was recovered and submitted once again to the same centrifugation procedure. The total concentration of free polymer chains in the supernatant (C_p) was determined by titration of the total organic carbon (TOC) using a TOC Carbon Analyser DC-80 (Tekmar Dohrmann). The same experimental procedure was used for each polymer concentration and two measurements were made each time.

Sample Preparation

Hybrid samples were prepared by mixing silica suspension with copolymer solution initially equilibrated at pH = 8. Due to the strong interaction taking place between copolymer chains and silica particles, the mixtures were kept under gentle stirring for 10 days and then at rest during 3 additional days before taking them for experiments. In these conditions, the viscoelastic properties were reproducible for all the mixtures studied up to $C_p = 20\,g\,L^{-1}$.

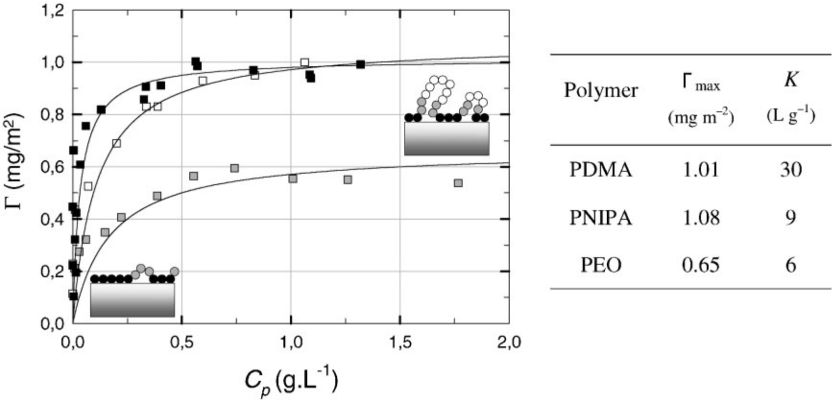
Rheology

Measurements of the viscoelastic properties of aqueous copolymer solutions, without or with added silica particles (0-140 g L^{-1}), were carried out on a controlled stress rheometer (Haake RS150) using a cone/plate geometry. The temperature was adjusted by a high-power Peltier system that provided fast and precise control of the temperature during the heating and cooling cycles. In order to explore a wide range of viscoelastic properties, the experimental conditions were fixed, after a first investigation of the linear domain, at $\sigma = 1$–5 Pa and constant frequency (f = 1 Hz). In these conditions, storage (G') and loss (G'') moduli as well as complex viscosity (η^*) were recorded within a temperature range from 20 to 60 °C (heating rate = 2 °C min^{-1}). Complementary experiments were also performed by scanning the frequency in the linear domain at a given temperature.

Results and Discussion

Adsorption Isotherm of Polymeric Grafts on Silica Particles

As previously mentioned, the same procedure has been applied for the adsorption experiments of PDMA, PNIPA and PEO on silica beads and we provided sufficient time (72 h) for adsorption and reorganization of the chains on the surfaces. The amount of adsorbed polymer on silica surfaces (Γ in mg m^{-2}) is plotted against the equilibrium polymer concentration in Figure 2. These isotherms immediately give evidence that both PDMA and PNIPA interact more energetically than PEO with silica surfaces. In the case of PDMA and PNIPA, we observe a strong adsorption regime at low coverage of the particles, with a sharp increase of the adsorbed amount of polymer for $\Gamma/\Gamma_{max} < 0.5$ ($\Gamma < 0.5$-0.7 mg m^{-2}). As previously reported from calorimetric analyses performed on PNIPA/silica mixtures,[24] this first regime corresponds to the adsorption of PNIPA (or PDMA) chains in a flat conformation (high proportion of trains compared to loops and tails) with a maximum of monomer units interacting directly with SiOH groups. This regime is followed by a weaker interaction domain ($\Gamma/\Gamma_{max} > 0.5$) where the adsorption of polymer chains involves a decreasing fraction of trains with the formation of larger loops and tails. This regime ends up at the plateau value, which is approximately the same for the two polymers: $\Gamma_{max} \cong 1$ mg m^{-2}. It corresponds to a silica/polymer weight ratio $W^0_{Si/Polymer} \cong 12$. The same holds for PEO chains but with a smaller extent as the plateau value is reached at $\Gamma_{max} \cong 0.6$ mg m^{-2} ($W^0_{Si/PEO} \cong 20$). These maximum amounts are in good agreement with those determined for similar systems.[25–26]



Polymer	Γ max (mg m^{-2})	K (L g^{-1})
PDMA	1.01	30
PNIPA	1.08	9
PEO	0.65	6

Figure 2.
Adsorption isotherms of PDMA (■), PNIPA (□) and PEO (▨) on silica particles at T = 20 °C. The solid lines are the theoretical fits obtained from the Langmuir isotherm: $\Gamma^{-1} = \Gamma_{max}^{-1}\left(1 + K^{-1}C_m^{-1}\right)$, with Γ_{max} the maximum amount adsorbed and K the Langmuir equilibrium constant.

As theoretically described by Scheutjens and Fleer,[27] the amount of non ionic polymers adsorbed at liquid/solid interfaces mainly depends on their affinity for the surface and their molecular weight. In the present case, the lower adsorbed amount of PEO can be attributed to its lower molecular weight (or DP_n) as compared to that of the poly(N-alkylacrylamide)s, and also to the lower efficiency of the oxide, compared to the carbonyl, to establish hydrogen bonds with silanol. Using the results obtained from the Langmuir isotherm model applied in the high coverage regime ($\Gamma/\Gamma_{max} > 0.5$, Figure 2), we can see that the adsorption equilibrium constant (K) increases from PEO to PNIPA and then to PDMA: $K = 3$, 6 and 30 L g^{-1}, respectively. In that case, the larger binding energy of adsorption for PDMA compared to PNIPA can be correlated to the higher strength of proton acceptor (or higher polarizability) of the carbonyl group in the disubstituted amide compared to the monosubstituted one.

Hydrogel Formation Between 2-PAMH-*g*-PDMA and Silica Nanoparticles

The viscoelastic properties of hybrid mixtures "2-PAMH-*g*-PDMA/silica/H_2O" were studied at $T = 20\,^{\circ}C$ for a large range of silica and copolymer concentrations. Starting initially with binary systems of very low viscosity, either copolymer solutions or silica suspensions, a tremendous increase of viscoelasticity was observed when organic and inorganic materials were mixed. An example is given in Figure 3 for a copolymer solution at $C_p = 20\,g\,L^{-1}$, with a crossover between dynamic moduli taking place at about $C_{Si} = 20\,g\,L^{-1}$.

This rheological behavior clearly gives the evidence for the formation of hybrid networks resulting from graft copolymer chains interconnected through inorganic cross-linkers. At a low concentration of added silica particles ($C_{Si} < 20\,g\,L^{-1}$), the number of inorganic junctions between polymer chains remains too low to reach the percolation threshold and the solution behaves mainly as a viscous liquid with isolated clusters. At $C_{Si} = 18\,g\,L^{-1}$, where G' and G'' follow the same frequency dependence (see inset of Figure 3), the mixture reaches the gel point (C_{Si}^{Gel}) according to the criterion of Winter et al.[28] At higher silica concentrations, the hybrid mixtures mainly behave as chemical gels with dynamic moduli exhibiting only very weak frequency dependence

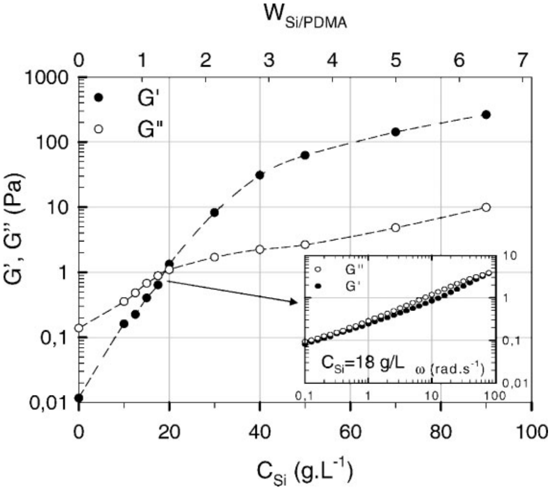


Figure 3.
Dependence of dynamic moduli G' (●) and G'' (○) with added silica concentration C_{Si} (or silica/PDMA weight ratio, $W_{Si/PDMA}$) for a solution of 2-PAMH-*g*-PDMA ($C_p = 20\,g\,L^{-1}$, f = 1 Hz and $T = 20\,^{\circ}C$). The inset gives the frequency-dependence of dynamic moduli close to the gel point ($C_{Si} = 18\,g\,L^{-1}$, $C_p = 20\,g\,L^{-1}$ and $T = 20\,^{\circ}C$).

with no relaxation process at our experimental conditions.

The gelation threshold being defined ($C_{Si}^{gel} = 18\,\mathrm{g\,L^{-1}}$), the viscosity and the plateau modulus can be plotted under reduced form using the relative distance from the gel point: $\varepsilon_{Si} = \left|\left(C_{Si} - C_{Si}^{gel}\right)/C_{Si}^{gel}\right|$ (Figure 4).

As predicted by the percolation theory, the viscosity and the plateau modulus scale with the reduced concentration, just before ($\eta \sim \varepsilon_{Si}^{-s}$) and after the gel point ($G_0 \sim \varepsilon_{Si}^{t}$), respectively. Here, the scaling exponents s = 0.79 and t = 1.85 are in good agreement with the theoretical values calculated in the framework of the electrical network analogy: s = 0.75, t = 1.9. This model lies on the analogy suggested by de Gennes between the elasticity of an incomplete network of springs and the conductivity of a percolating conductor network embedded in an insulating medium.[29] In the present case, the formation of hybrid hydrogels can be seen as the percolation of macromolecular chains through inorganic cross-linkers or, conversely, as the percolation of inorganic clusters through macromolecular connectors. By using the concentration of inorganic cross-linkers as the main variable, we can see that the percolation model describes the formation of nanocomposite hydrogels fairly well, irrespective of the copolymer concentration (see Table 2).

Table 2.
Silica concentration threshold (C_{Si}^{gel}) and scaling exponents ($G_0 \sim \varepsilon_{Si}^{t}$) for the sol/gel transition in ternary hybrid mixtures: 2-PAMH-*g*-PDMA/silica/H_2O.

C_p (g L^{-1})	C_{Si}^{gel} (g L^{-1})	t
20	18	1.85
10	12.5	1.79
7.5	10	1.68
5	8	1.97

As observed in Table 2, the silica concentration threshold (C_{Si}^{gel}) progressively decreases with decreasing copolymer concentration, but one can easily realize that below a certain silica concentration, the polyelectrolyte chain will not be large enough to bridge silica particles and to form a percolated network. By using the schematic representation given in Figure 5, one can estimate this critical silica concentration by equating the distance between silica surfaces ($d_{Si\text{-}Si}$) to the size of the polyelectrolyte chain (L)[31]:

$$d_{Si-Si} = (m_{Si}/C_{Si})^{1/3} - 2R_{Si} = L = Nb\left(l_B/bA^2\right)^{2/7} \quad (1)$$

with $m_{Si} = 3.3 \times 10^{-17}$ g the weight of a silica particle, C_{Si} the silica concentration, $R_{Si} = 15\,\mathrm{nm}$ the average radius of silica beads, $N = 840$ the degree of polymerization

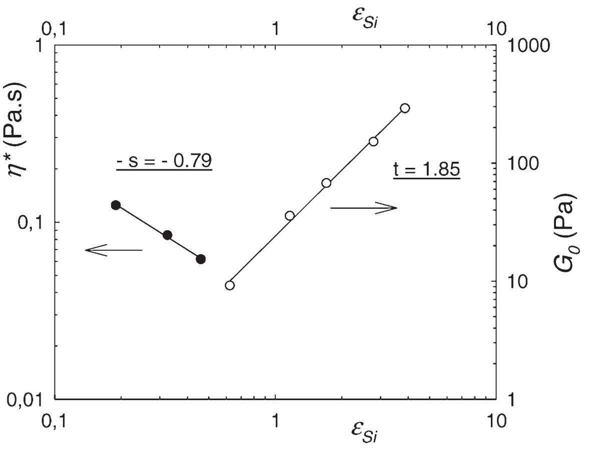


Figure 4.
Variation of viscoelastic parameters, G_0 (○) and η^* (●), against the reduced silica concentration for 2-PAMH-*g*-PDMA/silica/H_2O mixtures ($C_p = 20\,\mathrm{g\,L^{-1}}$; T = 20 °C).

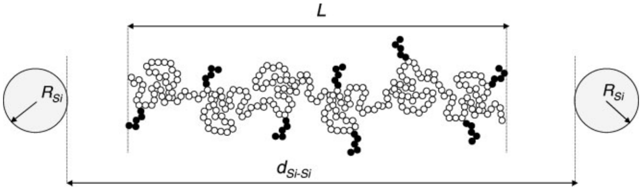


Figure 5.
Schematic comparison between the average distance between silica surfaces ($d_{Si\text{-}Si}$) and the size of the polyelectrolyte chains (L).

of PAMH, $b = 0.25\,\mathrm{nm}$ the size of the monomer, $l_B = 0.71\,\mathrm{nm}$ the Bjerrum length and $A = 3$ the average number of monomer units between two charges in the polyelectrolyte chain.

Under this assumption, we get a critical value $\left(C_{Si}^{Gel}\right)_{\min} = 6\,\mathrm{g\,L^{-1}}$ which is in good agreement with the series of gel points given in Table 2.

The whole series of viscoelastic data, obtained from various concentrations of copolymer ($C_p = 1, 2, 5, 7.5, 10$ and $20\,\mathrm{g\,L^{-1}}$) and silica particles ($C_{Si} = 10, 15, 20, 30, 40, 50$ and $90\,\mathrm{g\,L^{-1}}$), is given in Figure 6. Here, the complex viscosity of the ternary mixtures, normalized by the viscosity of the copolymer solution without added silica (η^*/η_0^*), has been plotted in a 2D mapping against copolymer and silica concentrations. This representation clearly shows the relative influence of organic and inorganic materials on the self-assembling behavior of the ternary mixtures. By adding a small amount of particles into the copolymer solutions, the mixtures rapidly turn from liquid solutions to viscoelastic gels, and we can see on the left side of the diagram that the sol/gel transition line fits approximately with a 10-times increase of the complex viscosity. The same holds when a small amount of copolymer is added into the silica suspension and the mixture rapidly becomes viscoelastic

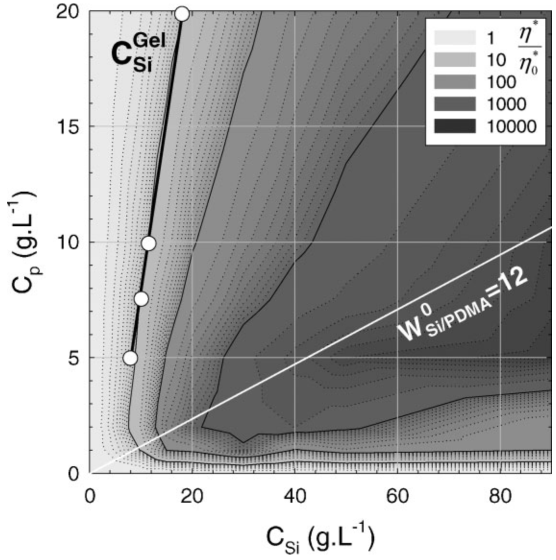


Figure 6.
Projection of the complex viscosity of the ternary mixtures, normalized by the viscosity of the copolymer solution (η^*/η_0^*), against copolymer and silica concentrations. The black line gives the limits of the sol/gel transition reported in Table 2, whereas the white line indicates the silica/PDMA weight ratio obtained from the plateau value of the adsorption isotherm.

above $C_p = 1\,g\,L^{-1}$. Moreover, if one compares the rise of viscosity obtained by mixing the graft copolymer with the silica nanoparticles, there is a range of optimal formulations that corresponds approximately to the "stoichiometry" of the complex silica/PDMA as determined from the adsorption isotherm ($W^0_{Si/PDMA} = 12$; white line in Figure 6).

The same results are also plotted in a normalized form in Figure 7 in order to emphasize the role of relative amounts of inorganic and organic materials on the gel properties. Again, the viscosity of the network is strongly correlated to the "stoichiometry" of the hybrid hydrogel resulting from the adsorption of PDMA onto silica particles. As a matter of fact, the viscosity maximum is effectively observed, for each series experienced at a given silica concentration, in the range of $W/W^0 = 0.6 - 1.2$. Below that range, there are less silica beads that are able to bridge copolymer chains through PDMA stickers and the viscoelastic properties progressively fall down. In the middle range ($W \cong W^0$), close to the saturation of silica surfaces by PDMA stickers, all the conditions are applied to get the maximum number of connections between silica surfaces and PDMA stickers. On the contrary, with an excess of silica particles ($W >> W^0$) there will be less polymer chains available to percolate the inorganic particles and the hydrogel will progressively become weaker, eventually with the formation of isolated aggregates.

This general feature is very similar to the case of hydrophobically modified polymer solutions in the presence of added surfactants[30] wherein the role of silica beads is played by the surfactant micelles which are able to bind hydrophobic stickers from different copolymer chains.

As the graft copolymer 2-PAMH-*g*-PDMA is fully hydrophilic (backbone and grafts), the temperature is not expected to have a strong effect on the macromolecular conformation but provides a good tool to probe the dynamics of the physical cross-links. In the case of hybrid networks, built from aqueous solutions of 2-PAMH-*g*-PDMA at $C_p = 10\,g\,L^{-1}$, the temperature dependence of the complex viscosity is rather weak, all the slopes being almost the same for different concentrations of silica (see Figure 8). This result can appear rather inconsistent as the activation energy (E_a) for viscous flow ($\eta \sim \exp(E_a/RT)$) normally scales with the binding energy and the strength of the physical interactions. In the case of strongly associating systems, as it is with the adsorption of PDMA stickers onto silica surfaces, a high viscosity with a large

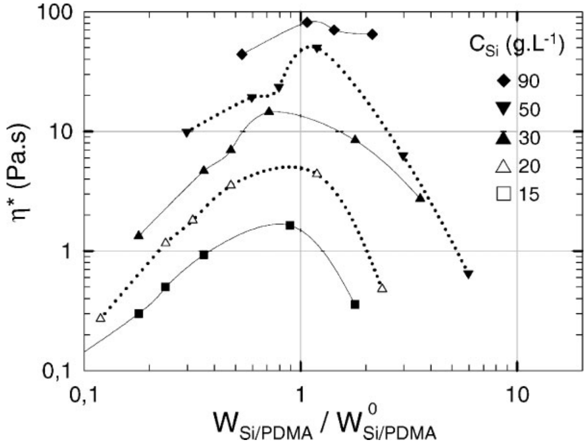


Figure 7.
Variation of the complex viscosity (f = 1 Hz) of hybrid mixtures for different weight ratio of silica/PDMA ($W_{Si/PDMA}$) normalized by the plateau value ($W^0_{Si/PDMA}$).

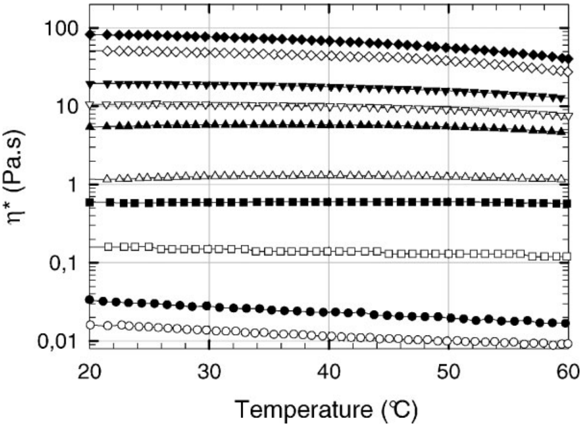


Figure 8.
Temperature-dependence of the complex viscosity η^* (f = 1 Hz) of aqueous mixtures of 2-PAMH-*g*-PDMA ($C_p = 10\ g\ L^{-1}$) prepared with increasing concentrations of silica ($g\ L^{-1}$): 0 (○); 5 (•); 12.5 (□); 17.5 (■); 20 (Δ); 30 (▲); 40 (▽); 50 (▼); 70 (◇); 90 (◆).

temperature dependence are normally expected. Nevertheless, if the interactions are too strong, their dynamics can be out of scale compared to our experimental conditions (f = 1 Hz). In other words, if the life time of physical associations is much larger than the characteristic time of the experiment, the associations seem to be permanent as in the case of a covalent network. This is exactly what happens with these hybrid mixtures; the activation energy remaining the same for all the systems and generally close to the solvent value (18-20 kJ mol^{-1}).

The data plotted in Figure 8 are in fact very similar to the ones we can get with solutions of non-associating polymers of different molecular weights (but similar concentration): the viscosity increases with the molar mass (here with the degree of binding) but the activation energy remains the same for all the systems and close to the activation energy of the solvent itself which is the main component at these concentrations (18-20 kJ mol^{-1} for water).

Hydrogel Formation Between 1-PAMH-*g*-PNIPA and Silica Nanoparticles

The associating behavior of PAMH-*g*-PNIPA with silica particles has been reported in detail in a previous study[23] and we will summarize in the present paper the main characteristics of those mixtures in order to draw a general comparison with other graft copolymers. As shown in Figure 9, the dynamic behavior of 1-PAMH-*g*-PNIPA with added silica is very close to the one previously depicted for PAMH grafted with PDMA (see Figure 3). For $C_p = 20\ g\ L^{-1}$, the percolation threshold of the hybrid mixture can be extrapolated at $C_{Si} = 35\ g\ L^{-1}$ following the criterion of Winter et al.[28] In these conditions, the plateau modulus (G_0) scales with the relative distance to the gel point (ε_{Si}) with an exponent t = 2.16 which is in good agreement with the percolation theory (electric network analogy).

The gel point and the power exponents extrapolated for different copolymer concentrations are reported in Table 3.

As previously observed with 2-PAMH-*g*-PDMA, the silica concentration threshold (C_{Si}^{gel}) decreases with decreasing copolymer concentration but the gel point remains higher with the copolymer grafted with PNIPA. This can be explained by a smaller size of the polymer backbone 1-PAMH ($DP_n = 540$), compared to 2-PAMH ($DP_n = 840$), and its lower ability to bind silica beads at long distances. By comparison with the previous calculation made from Equation {1} with solutions of 2-PAMH-*g*-PDMA ($(C_{Si}^{Gel})_{\min} = 6\ g\ L^{-1}$), we

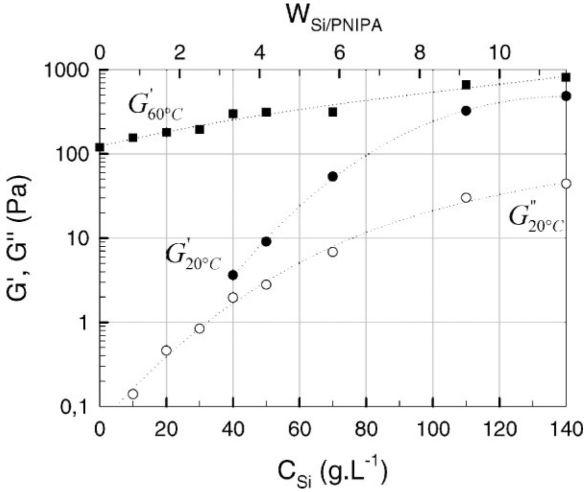


Figure 9.
Dependence of dynamic moduli G' (filled symbols) and G'' (open symbols) with added silica concentration C_{Si} (or silica/PNIPA weight ratio $W_{Si/PNIPA}$) for a solution of 1-PAMH-*g*-PNIPA ($C_p = 20$ g L^{-1}, f = 1 Hz) at T = 20 °C (circles) and T = 60 °C (■).

can extrapolate for 1-PAMH-*g*-PNIPA solutions a minimum value for the percolation threshold: $\left(C_{Si}^{Gel}\right)_{\min} = 16\,\mathrm{g\,L^{-1}}$, which is in good agreement with the other gel points reported in Table 3.

The collection of data obtained with hybrid mixtures at various concentrations of 1-PAMH-*g*-PNIPA and silica are plotted in Figure 10 using the reduced silica/PNIPA weight ratio.

As previously described with the PDMA derivative, the variation of viscoelastic properties is strongly correlated with the adsorption properties of the PNIPA side-chains. As a matter of fact, the maximum values of the viscosity are obtained close to the saturation of silica beads by PNIPA grafts ($W \approx W^0$), and this holds irrespective of the copolymer concentration. This specific feature, that correlates the local properties and the macroscopic ones, appears clearly as an intrinsic characteristic of the hybrid self-assemblies.

Table 3.
Silica concentration threshold (C_{Si}^{gel}) and scaling exponents ($G_0 \sim \varepsilon_{Si}^{t}$) for the sol/gel transition in ternary hybrid mixtures: 1-PAMH-*g*-PNIPA/Silica/H_2O.

C_p (g L^{-1})	C_{Si}^{gel} (g L^{-1})	t
20	35	2.16
10	25	1.88
5	~25	2.08

Finally, the main difference arising with hybrid mixtures of the copolymer grafted with PNIPA is their temperature dependence (see Figure 11). In the low temperature range (below 36 °C), the complex viscosity dramatically increases with the silica content (4 orders of magnitude with $C_{Si} = 140\,\mathrm{g\,L^{-1}}$) while all the mixtures display very similar slopes for the temperature dependence of the viscosity. As previously described for 2-PAMH-*g*-PDMA, this behavior can be attributed here to the strong interactions taking place between PNIPA and silica surfaces. Without added silica, the phase transition of PNIPA side-chains takes place above 36 °C and the self-assembling process gives rise to a sharp increase of viscosity above this temperature with a sol/gel transition induced by heating (thermothickening behavior).[23] In the presence of silica particles, hybrid connections are already formed at low temperature and it was shown[23] that NIPA units which are strongly adsorbed onto silica surfaces no longer participate in the transition process driven by the temperature.

Consequently by working at a fixed copolymer concentration, the number of

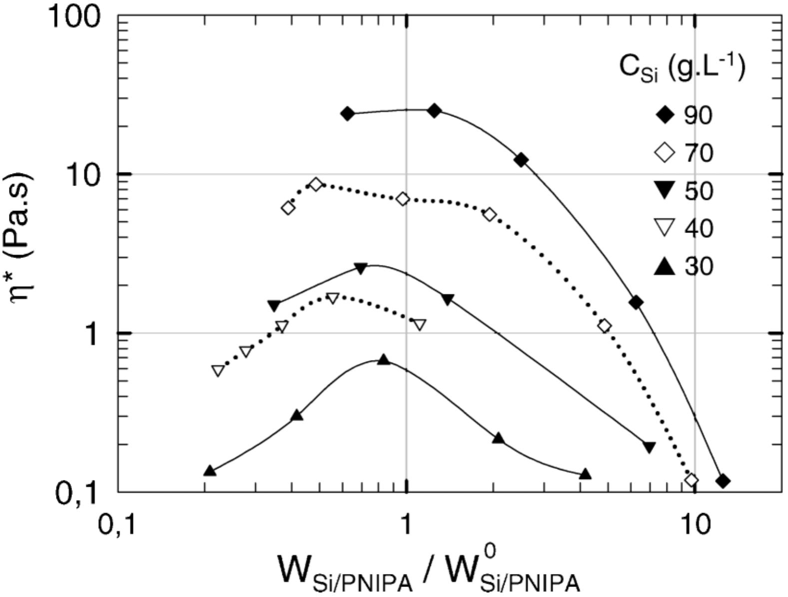


Figure 10.
Variation of the complex viscosity (f = 1 Hz) of hybrid mixtures for different silica/PNIPA weight ratios ($W_{Si/PNIPA}$) normalized by the plateau value ($W^0_{Si/PNIPA} = 12$).

"free" NIPA units which could effectively participate in the thermoassociating behavior progressively decreases with the silica content. The main consequences observable in Figures 9 and 11 are (i) the increase of the association temperature (from $T = 36\,°C$ at $C_{Si} = 0\,g\,L^{-1}$ to $T = 44\,°C$ at $C_{Si} = 140\,g\,L^{-1}$) and (ii) the decrease of the thermothickening effect ($\eta^*_{60°C}/\eta^*_{20°C}$ or $G'_{60°C}/G'_{20°C}$). At high silica concentration ($C_{Si} = 140\,g\,L^{-1}$ in Figures 9 and 11) the thermothickening remains very weak as most of the PNIPA grafts are involved in the formation of hydrid connections. We can extrapolate that below the saturation of silica surfaces by PNIPA grafts, i.e. at high

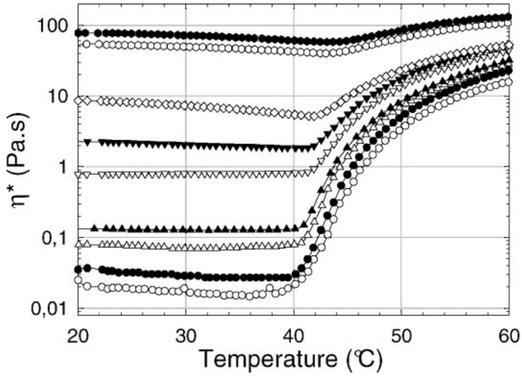


Figure 11.
Temperature dependence of the complex viscosity η* (f = 1 Hz) of aqueous mixtures of 1-PAMH-*g*-PNIPA ($C_p = 20\,g\,L^{-1}$) prepared with increasing concentrations of silica ($g\,L^{-1}$): 0 (○); 10 (•); 20 (Δ); 30 (▲); 40 (▽); 50 (▼); 70 (◇); 110 (⬡); 140 (⬢).

silica concentrations ($W > W^0$), the thermoassociating behavior will no longer exist.

In the case of hybrid mixtures "1-PAMH-*g*-PNIPA/silica/H_2O" studied at high temperature, the self-assembling behavior can be summarized by the formation of a conetwork with both inorganic (silica) and organic (PNIPA micelles) cross-links. These two contributions can be adjusted by the weight ratio between silica particles and PNIPA side-chains, with limits corresponding either to a single organic network at $W_{silica/PNIPA} = 0$ or a purely hybrid one for $W_{silica/PNIPA} > 12$.

Hydrogel Formation Between 1-PAMH-*g*-PEO and Silica Nanoparticles

The dynamic behavior of hybrid mixtures "1-PAMH-*g*-PEO/silica/H_2O" is shown in Figure 12 for three copolymer concentrations and increasing concentrations of silica particles.

Similarly to other graft copolymers, the hybrid mixtures made of 1-PAMH-*g*-PEO clearly display two viscoelastic regimes: a viscous one (sol), corresponding to $\tan\delta > 1$ ($G'' > G'$), and an elastic one (gel) where $\tan\delta$ becomes smaller than 1 ($G'' < G'$). Using $G' = G''$ ($\tan\delta = 1$) as a rough estimation of the transition threshold, we can see that C_{Si}^{Gel} increases with increasing copolymer concentration. The main difference between 1-PAMH-*g*-PEO and the other graft copolymers arises when the formulations are heated (Figure 13). As a matter of fact, the temperature dependence of the viscosity of hybrid mixtures rapidly increases with the concentration of silica particles. The activation energy extrapolated from the Arrhenius plot ($Ln(\eta) \sim (E_a/RT)$) increases from 18 kJ mol^{-1} (without added silica) to 35 kJ mol^{-1} (for C_{Si}= 70-110 g L^{-1}). Contrary to poly(*N*-alkylacrylamide) grafts which bind very strongly to silica surfaces, with possible rearrangements which are out of scale in our experimental conditions, the increase of the activation energy depicted in Figure 13 clearly underlines that within similar conditions the dynamics of the interactions taking place between PEO side-chains and silica surface are now observable.

Compared to poly(*N*-alkylacrylamide), these results underline the weaker interactions taking place between silica and PEO, as previously deduced from the adsorption isotherms. Very similar results were also obtained with copolymers grafted with polyether side-chains containing a high proportion of propylene oxide instead of ethylene oxide.[22] From a general point of view, this particular aspect is very important as it shows how the viscoelastic properties of hybrid networks are correlated to the thermodynamic properties of the binary system "adsorbing graft / silica

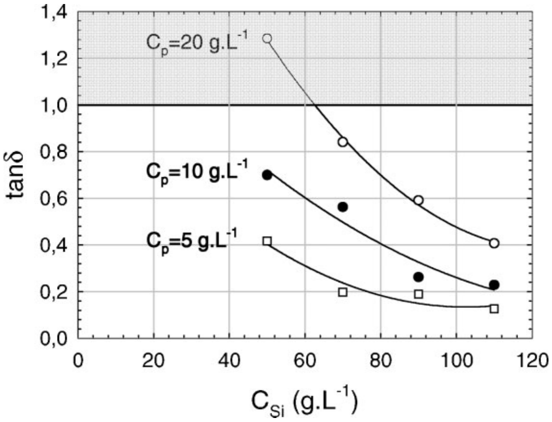


Figure 12.

Dependence of $\tan\delta = G''/G'$ with added silica concentration (C_{Si}) for solutions of 1-PAMH-*g*-PEO at various polymer concentrations: 5 g L^{-1} (□), 10 g L^{-1} (●) and 20 g L^{-1} (○) (f = 1 Hz and T = 20 °C).

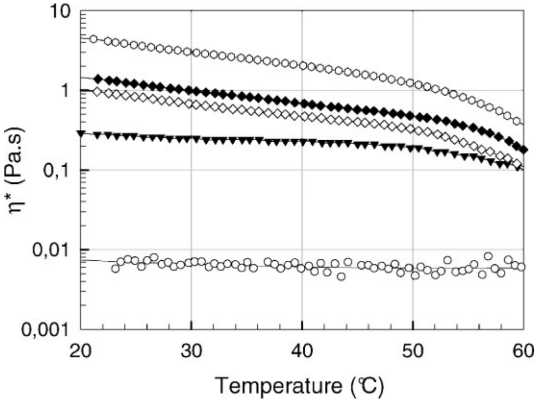


Figure 13.
Temperature dependence of the complex viscosity η^* (f = 1 Hz) of aqueous mixtures of 1-PAMH-*g*-PEO ($C_p = 5\,g\,L^{-1}$) prepared with increasing concentrations of silica ($g\,L^{-1}$): 0 (○); 50 (▼); 70 (◇); 90 (◆) and 110 (⬡).

surfaces''. For instance, the strength of the interactions between organic and inorganic materials will influence the dynamics of the network while the stoichiometry of the ''binary complex'' will control the architecture and the connectivity of the self-assembly.

This snapshot is emphasized in Figure 14 where the viscosity of hybrid formulations, prepared from the three different graft copolymers, has been plotted under reduced coordinates. The weight ratio between silica and grafts ($W_{Si/Graft}$) has been normalized by the plateau value of the adsorption isotherm ($W^0_{Si/Graft} = 12$ or 20 for poly(*N*-alkylacrylamide) or PEO, respectively) and the complex viscosities, determined at a given polymer concentration by varying the concentration of silica particles (see Figures 7 and 10), were reduced by the maximum value of viscosity obtained for each series.

As we can see, this normalization provides evidence on how hybrid mixtures self-assemble, irrespective of the nature of the graft copolymer or the concentrations of organic or inorganic materials. Here the ''stoichiometry'' of the adsorption process taking place between macromolecular side-chains and silica surfaces, appears

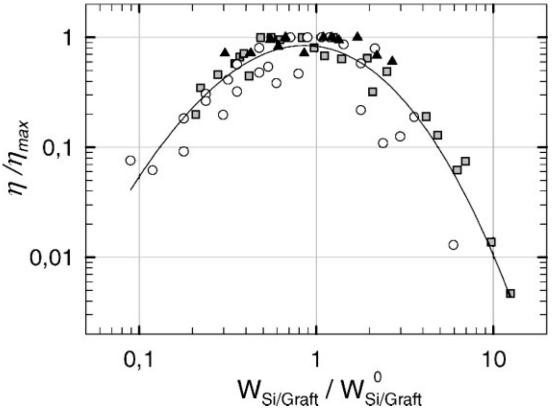


Figure 14.
Variation of the reduced viscosity (η/η_{max}) of hybrid mixtures for different silica/Graft weight ratio ($W_{Si/Graft}$) normalized by the plateau value ($W^0_{Si/Graft}$): 2-PAMH-*g*-PDMA (○), 1-PAMH-*g*-PNIPA (■) and 1-PAMH-*g*-PEO (▲).

undoubtedly as the central parameter which controls the viscoelasticity of hybrid hydrogels.

Conclusion

Based on specific interactions taking place between polymeric side-chains and inorganic nanoparticles, we demonstrate that hybrid hydrogels can be readily formed at low polymer concentration. Starting from different macromolecular systems, we show that a good knowledge of the binary complex ‘‘polymeric side-chain / particles’’ is essential to anticipate the viscoelastic properties of the physical network. The main parameter is the ‘‘stoichiometry’’ of the complex which can be obtained from the plateau value of the adsorption isotherm. As a matter of fact, the maximum amount of adsorbed side-chains per surface unit is a very good guide to optimize the viscoelastic properties of hybrid formulations. Below and above the ‘‘stoichiometry’’, the concentration of elastically active chains progressively decreases and the rheological behavior of hybrid mixtures turns from gel to sol when a large excess of organic or inorganic material is added. Moreover, we also point out that the dynamics of the physical network could be controlled through the strength of the interactions taking place between side-chains and silica surfaces. While copolymers tailored with polyether grafts display some relaxation process in our experimental conditions, the same backbone grafted with poly(*N*-alkylacrylamide) behaves like a covalent gel in the presence of silica nanoparticles.

In the case of graft copolymers designed with thermoresponsive PNIPA side-chains, we also show that at high temperature, the PNIPA grafts which are not adsorbed on silica surfaces are able to self-associate, forming a conetwork with both inorganic and organic cross-linkers.

Finally, we think that this set of data demonstrates the very general nature of this concept based on self-adsorbing graft copolymer onto nanoparticles. Within the context of this work, we specially focus on silica surfaces but clearly this can be extended to any kind of nanoconnectors, either inorganic or organic, and could find important applications in technologies involving anti-settling or thickening properties in complex formulations.

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