Gels

DOI: 10.1002/anie.200701757

Fast Multiresponsive Micellar Gels from a Smart ABC Triblock Copolymer**

Nicolas Willet, Jean-François Gohy, Liangcai Lei, Martine Heinrich, Loïc Auvray, Sunil Varshney, Robert Jérôme, and Bernard Leyh*

Self-assembly of block copolymers in a solvent selective for one block is at the origin of unique behaviors of micellar particles, such as stimuli responsiveness.[1–4] ABC triblock copolymers are very versatile precursors of micelles, whose internal structure is dictated by the constitutive blocks and their sequential arrangement. Accordingly, smart materials can be contemplated, including multiresponsive ones. Herein, we report on pH- and temperature-sensitive gels formed by an amphiphilic ABC triblock copolymer, polystyrene-*b*-poly(2-vinylpyridine)-*b*-poly(ethylene oxide). The self-assembly of this copolymer into core–shell–corona (CSC) micelles[5,6] is observed in *N*,*N*-dimethylformamide upon addition of water. The micellar solution forms a soft gel at a lower threshold copolymer concentration (8 wt %) than other systems.[7–9] This soft gel is reversibly converted into an optically clear hard gel by merely decreasing the pH value or increasing the temperature. The ordered packing of the CSC micelles and the fast response to pH value were investigated by small-angle neutron scattering (SANS) and rheological measurements.

Block copolymers consist of two or more chemically different polymer chains covalently bonded at their chain ends to form one single linear macromolecule.[10] The free-energy-driven micellization of these copolymers takes place in a selective solvent, that is, a nonsolvent for one block and a good solvent for another. This self-association phenomenon is based on the phase separation of the insoluble blocks, which is, however, restricted to the nanometric scale by a surrounding shell of soluble blocks. Depending on the nature, length, and number of constitutive blocks and their interaction with the solvent, a variety of nanoobjects can be formed in dilute solutions, ranging from typical core–shell nanospheres[11–13] to cylinders,[12,14] vesicles,[12,15,16] and tubules,[16] as well as multi-layered (onion),[5,17] non-centrosymmetric ("Janus"), and segregated structures.[18,19] Quite importantly, although less extensively studied, higher levels of organization can be observed, that is, assembly into clusters, networks, and gels. Stimulus-triggered aggregation of micelles has been reported for ABA triblock copolymers in a solvent selective for the B block,[9,20–24] with special attention paid to the well-known polyoxyalkylene-type ABA copolymers (mainly Pluronics).[9,20,21] Among other responsive systems, Armes and co-workers synthesized biocompatible ABA triblocks, where A is poly(*N*-isopropylacrylamide) and B is poly(2-methacryloyloxyethyl phosphorylcholine).[24] Because of the thermosensitivity of the outer A blocks, micellization and ultimately gelation occurred above a lower critical solution temperature (LCST) of 37 °C. In recent years, increasing attention was paid to sol-to-gel transitions exhibited by multitalented ABC terpolymers. In addition to the synthesis of several isomers of a triblock terpolymer (ABC, BAC, and ACB) by Patrickios and co-workers that were tested as emulsion stabilizers,[25,26] Aoshima and co-workers investigated an ABC copolymer that formed micelles, then formed a gel, and finally precipitated in water with increasing temperature.[27] Tsitsilianis and co-workers studied the pH-sensitive self-organization of highly asymmetric ABC copolymers in water from micelles to 3D networks.[28,29] Temperature-sensitive ABC triblock copolymers were studied by Hamley and co-workers. These systems, however, proved to be moderately effective gelators, with a required copolymer concentration around 20 wt %.[30] Herein, we report the first bottom-up demonstration of a multiresponsive gel made from original micellar self-assemblies.

We describe the preparation and investigation of three-component micellar gels endowed with stimuli-responsive properties. For this purpose, an amphiphilic ABC terpolymer,

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[*] N. Willet, L. Lei, Prof. R. Jérôme
Center for Education and Research on Macromolecules (CERM)
University of Liège
Sart-Tilman, B6, 4000 Liège (Belgium)
Fax : (+32) 4-366-3497
E-mail: rjerome@ulg.ac.be
Homepage: http://www.ulg.ac.be/cerm

Prof. J.-F. Gohy
Unité de Chimie des Matériaux Inorganiques et Organiques (CMAT)
Université catholique de Louvain
Lavoisier, place Pasteur 1, 1348 Louvain-la-Neuve (Belgium)

Dr. M. Heinrich
Institut für Festkörperforschung (IFF)
Forschungszentrum Jülich (Germany)

Dr. L. Auvray
Laboratoire Léon Brillouin (LLB)
CEA Saclay (France)

Dr. S. Varshney
Polymer Source Inc.
124 Avro Street, Dorval (Montreal), Quebec H9P 2X8 (Canada)

Prof. B. Leyh
Laboratoire de Dynamique Moléculaire
University of Liège
Sart-Tilman B6, 4000 Liège (Belgium)

[**] The authors are much indebted to the "Politique Scientifique Fédérale" for financial support through the program "Interuniversity Attraction Poles Programme (PAI VI/27): Functional Supramolecular Systems", and to the European Commission for financial support and access to the Forschungszentrum Jülich ("Jülich Neutrons for Europe") and the Laboratoire Léon Brillouin (Saclay, France). J.-F.G. is grateful to the ESF "STIPOMAT" Program.

polystyrene-*b*-poly(2-vinylpyridine)-*b*-poly(ethylene oxide) (PS_{200}-*b*-$P2VP_{140}$-*b*-PEO_{590}, where subscripts refer to the average degree of polymerization of each block), was synthesized. The key features of this copolymer are amphiphilicity and multiresponsiveness. Indeed, the PS block is hydrophobic, whereas the PEO block is hydrophilic with a water solubility that depends on temperature, and the central P2VP block is either hydrophilic or hydrophobic, depending on pH value of the medium. The synthesis relies on the sequential living anionic polymerization of styrene, 2-vinylpyridine, and ethylene oxide. The polydispersity index of this well-defined terpolymer is as low as 1.10.

In pure water and at room temperature, it was reported that approximately 120 copolymer chains self-associate per core–shell–corona (CSC) micelle.[6] Indeed, a hydrophobic core of PS is surrounded by a dense P2VP shell that is extended by a corona of expanded water-soluble PEO chains. Because of the propensity of the 2VP units to be protonated, these CSC micelles are sensitive to pH value, which accounts for the reversible tuning of the average hydrodynamic diameter (D_h) from 75 nm at neutral pH values to 135 nm at acidic pH values. This important size modification is due to the stretching of the P2VP and PEO blocks, as determined by light- and neutron-scattering techniques. Additionally, the core–shell–corona structure of the PS_{200}-*b*-$P2VP_{140}$-*b*-PEO_{590} micelles after evaporation was directly observed using TEM and AFM.[5] The characteristic diameter of the PS core (20 nm) and the thickness of the P2VP shell (7.5 nm at neutral pH and 15 nm at low pH) were determined accordingly in the dry state. These data suggest that the swelling of the PEO chains after protonation of the P2VP blocks results in an increase of the corona thickness of roughly 20 nm, which is expected to play a pivotal role in the gel behavior.

Whenever a small amount of water (e.g. 10 wt %) is added to a dilute solution of the PS-*b*-P2VP-*b*-PEO copolymer in DMF (e.g. 0.5 wt% of ABC copolymer), micellization occurs as a result of the loss of solubility of both the PS and the P2VP blocks. Moreover, at a somewhat higher copolymer concentration (8 wt %) in DMF, addition of water up to 10 wt % triggers the simultaneous formation of micelles and of a macroscopically homogeneous soft gel. Upon shearing in a Couette cell, a high storage modulus *G′* of 650 Pa is measured at a frequency of 1 Hz and a strain amplitude of 1 %. Furthermore, the pH value has an instantaneous, dramatic effect on the micellar gel after less than one second shaking. Indeed, as soon as $pH < 5$, that is, when the P2VP blocks are protonated and the micelles are mutually repulsive, the *G′* modulus jumps at once up to 1400 Pa, consistent with a hard gel containing expanded and entangled PEO chains (see Figure 1). Because the volume of the micelles increases when the pH value is lowered, a transition from short- to long-range order towards a more compact structure can occur upon protonation, provided that the specific volume of the gel does not change significantly. The *G′* values are very high, being from 5 to 100 times higher than the modulus of recently reported micellar gels.[8,22,23,30,31]

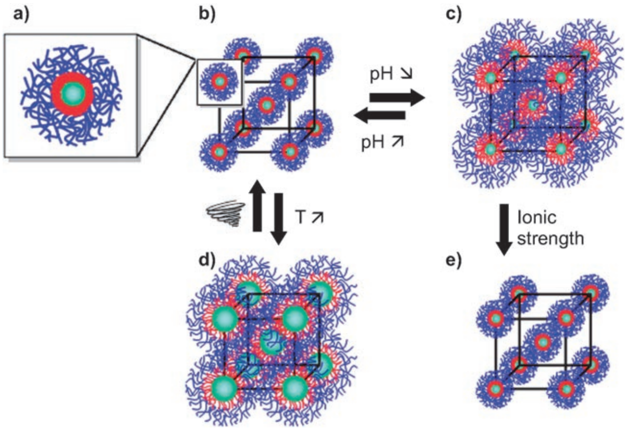

Figure 1. Schematic representation of the hierarchical organization and the action of stimuli: a) three-layer micellar substructure with a PS core surrounded by a P2VP shell and a PEO corona; b)→c): transition of the neutral micellar gel from short- to long-range order; c) hard-gel formation owing to PEO interpenetration and entanglement after protonation and reverse transition by neutralization; d) hard-gel formation owing to PS solvation after heating and reverse transition by applying shearing stress; e) transition back to soft gel by increasing the ionic strength and screening the repulsive electrostatic forces.

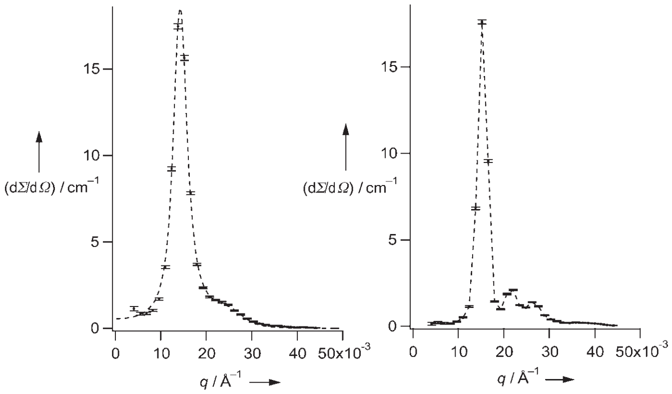

Figure 2. Scattering differential cross section per unit volume of the micellar gel at neutral pH (left) and with one added equivalent of HCl (right). These data were recorded on the PACE SANS diffractometer.[32]

In order to give credit to this mechanism, SANS scattering cross sections were recorded at neutral and decreasing pH values (Figure 2).[32] Fairly wide peaks are discerned at neutral pH (soft gel). A correlation length of (150 ± 5) nm (twice the hydrodynamic diameter) was calculated from the full width at half maximum of the first peak. The data are well fitted by the Percus–Yevick model for hard spheres in a fluid state.[33,34] A hard-sphere diameter of (49 ± 1) nm, a gyration radius of (12 ± 1) nm, and a micelle volume fraction of (0.44 ± 0.1) were calculated. As expected, the latter value is smaller than the equilibrium volume fraction for crystallized hard spheres,[35] which means that translational mobility is preserved at this point, and the gel flows freely.

Upon protonation with HCl (0.5 or 1.0 equivalent with respect to the 2VP units), peaks tighten (Figure 2, right), consistent with a correlation length of (280 ± 10) nm. These data no longer fit the hard-sphere model. Rather, they are consistent with a crystalline ordering according to a body-centered cubic structure (bcc), in line with the long PEO corona chains.[7] This structure has been confirmed by recent time-of-flight SANS measurements. The following structural parameters were deduced: a bcc cell parameter of (56.5 ± 0.5) nm and an intermicellar distance of (49.0 ± 0.5) nm, which is smaller than the diameter of the protonated micelles. The corona chains are thus compacted, which forces them to be interdigitated or entangled and accounts for the increase in both the elastic modulus measured by rheology and the micellar volume fraction from 0.44 (hard spheres, neutral pH) to 0.68 (bcc, acidic pH) measured by SANS. The system is then a free-standing hard gel.

Further increase in the proton activity (two equivalents HCl) results in a transition back to the soft gel originally observed at a neutral pH value. Wider peaks show up again, with a correlation length of 150 nm. The Percus–Yevick model again fits the data, with a micelle volume fraction of 0.42, a hard-sphere diameter of 54 nm, and a gyration radius of 14 nm. Upon increasing the ionic strength with an excess of HCl, the protonated 2VP sites are screened, the P2VP chains collapse on the PS core, and the PEO chain extension is concomitantly reduced. As a result, the PEO blocks of adjacent micelles are no longer interpenetrated, and the soft gel is restored. Ionic-strength-induced effects were previously reported for the PS-*b*-P2VP-*b*-PEO micelles in dilute aqueous solution.[5] Moreover, the transition from hard to soft gel can also be triggered by changing the pH value in the opposite direction to neutralize the protonated P2VP blocks. Indeed, addition of a strong base (KOH or LiOH) with vigorous shaking converts the pyridinium units into the neutral form with the simultaneous collapse of the P2VP blocks onto the PS cores of the micelles. This decrease in the micellar size allows the micelles to recover mobility and the gel to flow again.

In addition to pH value, temperature is an effective stimulus that triggers transition from a soft to a hard gel. Indeed, the medium rapidly turns into a free-standing gel as soon as the temperature reaches 80 °C (Figure 3). In contrast to the solubility of PEO, which was maintained at 80 °C, that of PS in the DMF/H_2O mixture changed with temperature. Indeed, the θ temperature, which indicates the transition from soluble to insoluble, of PS in this medium was found in the range 70–75 °C. At room temperature, polystyrene forms a compact micellar core, and no typical signal is detected by ^{1}H NMR spectroscopy. Above the θ temperature, at 80 °C, the resonances of the PS aromatic protons are observed as a consequence of PS solvation (see Figure 3). The swelling of the PS core at high temperature increases the micellar D_h, which remains monodisperse, as confirmed by dynamic light scattering (DLS). The expansion of the micelles triggers the intermicellar penetration and entanglement of the external PEO chains. Quite surprisingly, the gel remains free-standing upon cooling as long as no stress is applied, although the PS core shrinks when the temperature is decreased, as confirmed by ^{1}H NMR spectroscopy. The persistence of the hard gel during cooling at rest suggests the persistence of the intermicellar entanglement of PEO coronal chains. If this is the case, shearing the hard gel (vortex shaker) when it is cooled down might contribute to the disruption of the chain entanglements and allow the gel to recover its flowing properties. For this reason, heating–shearing cycles have been carried out, as illustrated in Figure 4. A reversible switching from flowing to free-standing gels and vice versa is typically observed. Indeed, after a first heating step up to 80 °C, G' and G'' (loss modulus) remain high when the gel is cooled down to 20 °C without shearing (left edge of the curves in Figure 4). Shearing at 1 Hz is then switched on together with a slow temperature increase (rate = +2.5 °C min^{-1}). A rapid softening of the gel (decrease of G' and G'') is observed, which can be unambiguously assigned to the shearing,

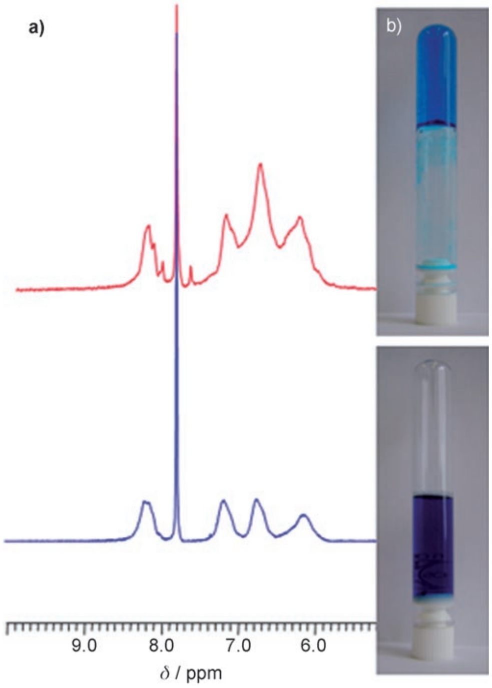

Figure 3. a) ^{1}H NMR spectra of PS aromatic protons for the soft gel at room temperature (bottom) and the free-standing hard gel after brief heating at 80 °C (top). Peaks between 8.0 and 8.5 ppm are typical of P2VP, and those between 5.7 and 7.7 are characteristic of both P2VP and PS. b) Digital photographs of the corresponding inverted test tubes colored with methylene blue.

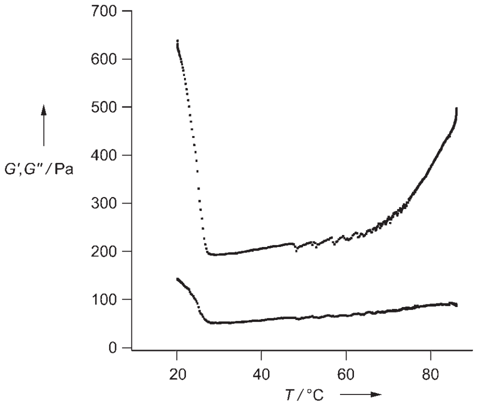

Figure 4. Evolution of G' (upper trace) and G'' (lower trace) with temperature. The gel sample was heated at 80 °C and cooled before the experiment without shearing. Absolute modulus values are intentionally slightly lower than usual, because a slight excess of water was added for experimental convenience.

because the gel is not temperature-sensitive in this range. The hard gel is restored when the sample is again heated up to 80 °C, which shows that shearing at high temperature leaves the hard gel intact.

In summary, CSC micelles of PS-*b*-P2VP-*b*-PEO in a DMF/water mixture self-organize into well-defined compact assemblies that have the consistency of a soft gel at a polymer content of 8 wt %, which is a very low value compared to other reported micellar gels.[7–9,22,30] Temperature increase to 80 °C and decrease of the pH value to pH 2 are two stimuli that trigger the conversion of this soft gel into a hard gel, which has a very high storage modulus. The response is extremely fast. Indeed, the response time is shorter than the time needed to change the pH value or the temperature. Starting from the hard gel at pH 2, addition of either excess acid or an aliquot of strong base also leads very rapidly back to a soft gel. Whenever temperature is the stimulus, an easy vortex shaking of the hard gel converts it to the soft flowing gel upon cooling. During all of these experiments, the medium remains optically clear. This transparency has important consequences for potential optical applications.[36,37]

Experimental Section

Materials: PS-*b*-P2VP-*b*-PEO copolymer was synthesized by sequential anionic polymerization of the comonomers, as reported elsewhere.[5] The molecular characteristics of the triblock copolymer used in this study are listed in Table 1.

Table 1: Molecular characteristics of the investigated ABC triblock copolymer.

	M_n (PS)	M_w/M_n (PS)	M_n (P2VP)	M_w/M_n (PS-*b*-P2VP)	M_n (PEO)	M_w/M_n (PS-*b*-P2VP-*b*-PEO)
PS_{200}-$P2VP_{140}$-PEO_{590}	20000	1.05	14000	1.05	26000	1.1

Preparation: The triblock copolymer (0.16 g) was added to *N*,*N*-dimethylformamide (DMF, 1.64 g) and warmed gently until complete dissolution. The clear solution was then rapidly added to MilliQ water (200 μL) and subsequently shaken vigorously (vortex shaker) until a homogeneous gellike solution was obtained. In the case of acid gels (for instance, from stoichiometric protonation), only 170 μL of MilliQ water were added prior to shaking, with subsequent acidification using 12 M HCl (30 μL, 1 equiv).

Rheology: Dynamic rheological measurements were carried out with an advanced rheometric expansion system (ARES) from Rheometrics. A Couette cell geometry was used with the following characteristic dimensions: cup diameter = 34 mm, bob diameter and length = 32 and 33 mm, respectively. Temperature programs were carried out at a shear frequency of 1 Hz and a strain of 1 %. Temperature was carefully controlled by a thermostatic bath. Heating rates of 2.5 °C min^{-1} from 20 to 70 °C and of 1 °C min^{-1} from 70 to 90 °C were used when appropriate. Because of a slight temperature gradient from the bath to the Couette cell, reported temperatures are those measured by a thermocouple in the cell.

Small-angle neutron scattering (SANS): Experiments were performed at the Orphée Reactor of the Laboratoire Léon Brillouin at Saclay (France) on the PACE diffractometer and on the KWS-2 instrument at the FRJ-2 reactor of the Forschungszentrum Jülich (Germany) at wavelengths of 10 and 6 Å, respectively, with a resolution $\Delta\lambda/\lambda \approx 10\,\%$. The data were collected on two-dimensional area detectors and radial averaged. Parasitic contributions of the electronic and ambient backgrounds and of the sample holder were eliminated by standard data-handling procedures. The scattering intensities were converted to macroscopic scattering cross sections per unit volume $d\Sigma/d\Omega$ (reported in cm^{-1}) based on a calibration with either poly(methylmethacrylate) (KWS-2) or the incoherent scattering of water (PACE).

Received: April 20, 2007
Revised: July 19, 2007

Keywords: copolymers · gels · micelles · self-assembly

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