Soft Matter

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Soft Matter

ARTICLE

Collapsing and reswelling kinetics of thermoresponsive polymers on surfaces: a matter of confinement and constraints

Nicolas Willet,*[a] Sabine Gabriel,[b] Christine Jérôme,[b] Filip E. Du Prez[c], and Anne-Sophie Duwez*[a]

We report on the collapsing and reswelling ability of grafted poly(methyl vinyl ether) chains of different molecular architectures. In order to study the influence of constraints and confinement of the chains, the polymer was grafted onto AFM tips, as a model of a curved nano-sized surface, and onto macroscopic silicon substrates for comparison purposes. AFM-based force spectroscopy experiments were performed to characterise at the nanoscale the temperature dependent collapsing process and the reversibility to the swollen state on both substrates. The reversible character of the thermoresponsive transition and its kinetics were shown to greatly depend on the polymer architecture and the constraints encountered by the chains.

Introduction

Stimuli-responsive systems are undoubtedly more and more in the limelight. This is especially true in the field of nanomaterials and polymer science where the topic is exponentially growing, with a broad range of advanced micellar [1-3] and vesicular systems,[4, 5] gels,[6, 7] membranes [8, 9] and brushes.[10, 11] Materials and devices able to give a specific response to external stimuli (temperature, pH, light, *etc*.) can play a major role in myriads of applications,[12] *i.a.* in the biomedical and pharmaceutical industry, in the field of (bio)separation, as intelligent switches or valves, as sensors and actuators. Among others, temperature-sensitive polymer materials have raised much attention lately. Poly(*N*-isopropylacrylamide) (PNIPAM),[13, 14] poly(*N*-vinylcaprolactam)[15, 16] and poly(ethylene oxide) functionalised methacrylates (*i.e.* POEGMA) [17, 18] are typical examples of thermoresponsive polymers. Poly(methyl vinyl ether) (PMVE) is another well-known polymer exhibiting a lower critical solution temperature (LCST) behaviour at about 37°C.[19] One of the interests for such polymers lies in the possibility to tune the hydrophilicity, wettability as well as the nanomechanical properties of surfaces, as a function of temperature. Below the LCST, polymer chains are swollen and form an expanded structure in aqueous solution, whilst above the LCST, chains collapse and form a more compact structure as a result of the rupture of hydrogen bonds with water by the thermal energy and the dehydrated molecules self-aggregate.[20] This behaviour in

solution has been extensively studied. Detailed investigations of the coil-to-globule transition have been published.[16] The presence of single chain globules, meso-globules or aggregates have been evidenced as a function of the polymer nature, polymer concentration, molar mass, heating rate, *etc*.

Studies on the behaviour of thermoresponsive polymers on surfaces have not been carried out with the same level of detail and completeness. The classical method that is widely used to characterise the behaviour on surfaces is contact angle measurements, which only provides indications about the hydrophilic or hydrophobic character of the surface. The problem of reversibility is also something that has been eluded in the literature. Most brush applications are for colloidal objects of spherical shape, and the reversibility and its dynamics are often crucial. However, responsive brushes for colloidal systems are an under-investigated field. A curved surface may strongly modify properties of the brushes since the volume available for the grafted chains is a function of the distance from the grafting surface and changes with curvature.[21]

Here, we report on AFM-based force spectroscopy investigations on the collapsing and reswelling ability of grafted PMVE chains. For this purpose, acrylic macromonomers of PMVE with different molecular architectures were synthesised by living cationic polymerisation,[22] providing mono-acrylate (PMVE-A ; Mn = 1100 g.mol⁻¹, Đ = 1.08) and bis-acrylate (A-PMVE-A ; Mn = 2300 g.mol⁻¹, Đ = 1.18) terminated linear chains (Scheme 1). Both types of macromonomers were subsequently grafted by

electro-initiated polymerisation on AFM tips and silicon substrates, following our previously reported procedure.[23-25]
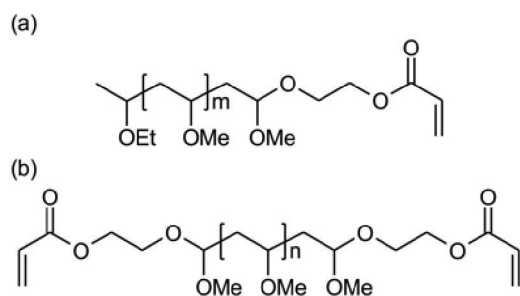
Scheme 1 Chemical structure of (a) PMVE mono-acrylate (PMVE-A) and (b) PMVE bis-acrylate (A-PMVE-A) macromonomers

By comparing the behaviour of the polymer grafted on the tips, which can be considered as models of a curved nano-sized surface, and on the macroscopic substrates, we intend to obtain information on the effects of confinement and constraints on the surface properties. The radius of the tip is about 20 nm. Previous theoretical investigations have shown that a radius below 50 nm has a very pronounced effect on the volume available for each chain.[26] The segment density was shown to be strongly reduced as compared to a flat surface.
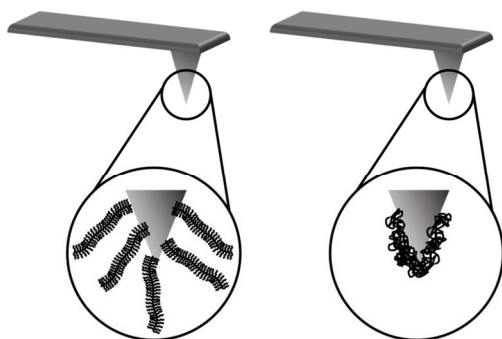

Fig. 1 Schematic view of AFM tips grafted with poly(PMVE) chains. Below the LCST (left), polymer chains are swollen in water, whereas after heating above the LCST (right), the chains dehydrate and collapse onto the AFM tip

Besides the chain architecture and the radius of the curved surface, the grafting density is also a parameter that strongly affects the responsiveness of polymer brushes.[21] At small grafting densities, the response of grafted chains is very similar to that of the bulk polymer solution. At high grafting densities, the collapse is weak because of the very crowded layer of strongly stretched polymer chains. There is thus very limited free space for conformational changes. In the grafting density regime between very low and high surface coverage, brushes show the most pronounced response to solvent quality. The largest conformational response is obtained in the very beginning of the brush regime when chains start to overlap.[21] We thus used grafting conditions (a monomer concentration of 0.1M, see methods section for details) to obtain a diluted regime.[24] We have previously shown that in those conditions, the grafting density was about 1 chain/100 nm^2.[24, 25] Both the

AFM tips and silicon substrates were prepared using the same grafting strategy and conditions.

Results and discussion

The cloud points of the macromonomers were checked in (1 wt%) aqueous solution prior to the grafting step, and were found to be 35.7 °C and 38.8 °C for PMVE-A and A-PMVE-A, respectively.

The behaviours of the different poly(PMVE)-grafted tips were studied by AFM operating in force-distance mode, both at room temperature and at 50°C, well-above the cloud-point temperature (Fig. 1). Both approach and retraction traces were carefully analysed. It is important to note that unbinding lengths and forces are not discussed here, as they are not useful to characterise the collapsed or swollen state of the polymer layer. Indeed, we and others have previously shown that the general shape of the whole force-distance trace, and especially during the approach phase when the polymer layer is getting trapped between the AFM tip and the substrate (the so-called compression profile), provides exquisite information about the quality of polymer layers, like the grafting density, thickness, swollen or precipitated states, *etc*.[24, 25, 27-29] Approach-retraction curves were recorded in water between the modified probes and a bare glass slide. Typical approach profiles at room temperature are shown in Fig. 2a and 2b (black curves).

In the case of poly(PMVE-A)-grafted AFM tips (Fig. 2a), the approach profile exhibits a slight force increase in the very low repulsive forces range. This increase is characteristic of the compression of an end-grafted polymer.[28, 29] The repulsive force is mainly caused by the reduced configurational entropy of the polymer chains upon increasing confinement.[28] However, as the contact with the glass surface is more and more pronounced, the curve starts to show irregularities. The profile does not follow a single exponentially decaying function characteristic of the compression of moderately dense brushes.[29] "Escape transitions", characteristic of the compression of isolated chains,[27] can be distinguished: the chains have enough space and lateral mobility to temporarily escape from the tip-surface region of compression, which is the typical behaviour for a very low grafting density.[24]

In the force curves obtained from poly(A-PMVE-A) (Fig. 2b), the expected signature for a brush of polymer chains swollen in a good solvent was observed,[29] *i.e.* an exponential increase of the force in the approach curves as the polymer is compressed between the tip and the glass slide. Such a smooth approach profile, which is typical for brushes in a good solvent, may seem surprising since we expect a low amount of polymer chains present at the tip apex. The explanation must be found in the presence of an acrylate moiety at each chain-end of the macromonomers. Upon electrografting, higher polymerisation rate and partial cross-linking are thus likely, probably leading to a gel-like structure and thus reduced chain mobility, even with few grafted chains.

Upon withdrawing functional tips from the glass slide, the interactions established between poly(PMVE) chains and the

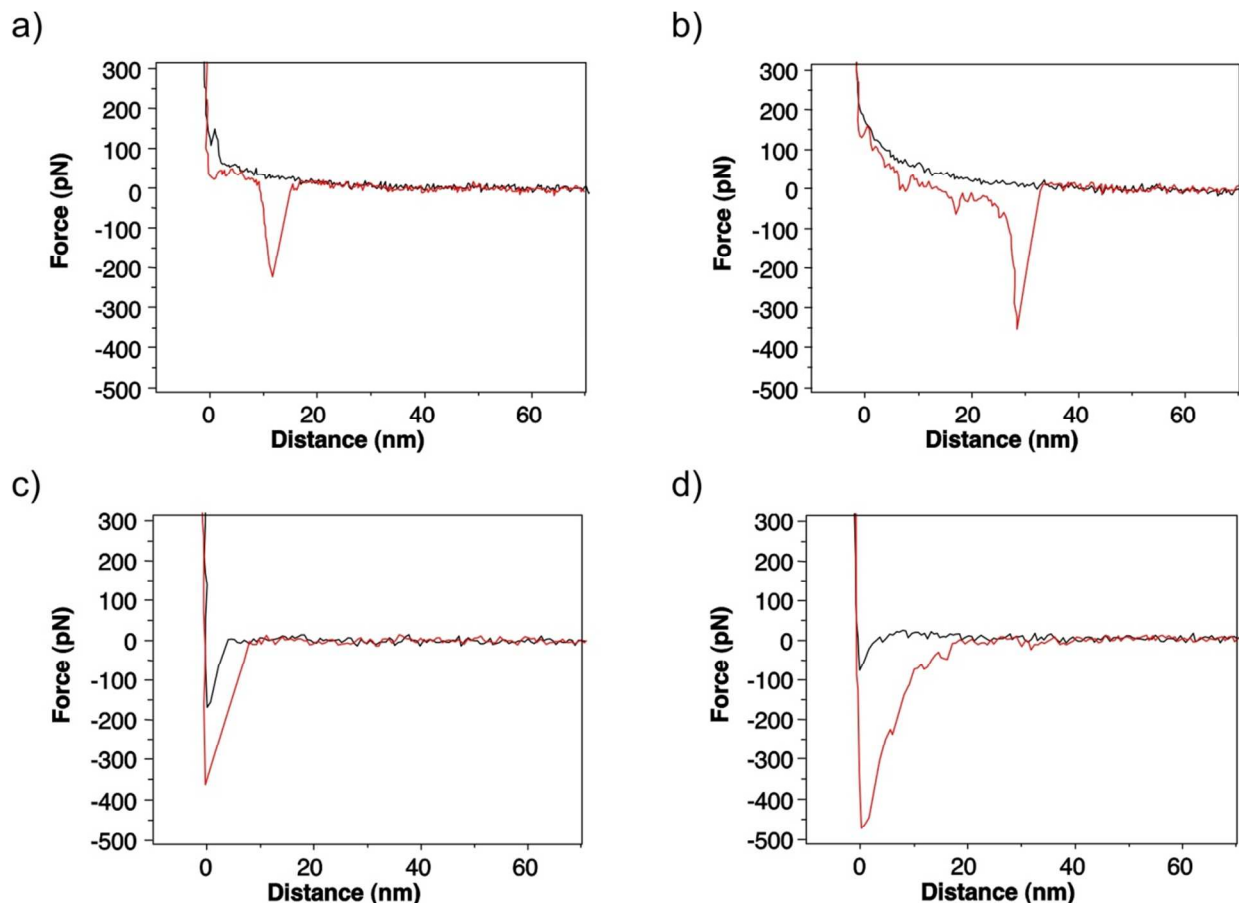# Soft Matter   RSC**Publishing**

Fig. 2 Examples of force-distance profiles (approach in black, retraction in red) obtained from the different thermoresponsive AFM probes in water. (a) Mono-acrylate PMVE tip below LCST. (b) Bis-acrylate PMVE tip below LCST. (c) Mono-acrylate PMVE tip above LCST. (d) Bis-acrylate PMVE tip above LCST

substrate during the contact are ruptured under load. The corresponding profiles display unbinding peaks with forces ranging from a few tens to a few hundreds of pN, typical of a physisorption process (Fig 2a and 2b, red curves). Most of the retraction curves for poly(PMVE-A) tips did not show any event, whereas 15% of them contained one single parabolic unbinding peak, which is a strong indication of individual chains with a low grafting density interacting with the surface (Fig. 2a). In the case of A-PMVE-A, the retraction profile shows several peaks and, in the short distance range, a deviation from the baseline, indicating the pulling of a bundle of chains (Fig. 2b, red curve). This observation confirms the expectations that the polymer chains are cross-linked, leading to a gel-like structure, which prevents the stretching of single macromolecules.

In order to investigate the ability of the tips to respond to temperature changes, the temperature in the liquid cell was

raised to 50 °C. AFM cantilevers were then exposed to the liquid cell and used directly for force spectroscopy. After some time, the collected force-distance curves drastically differed from the ones obtained without any heating step. Indeed, the compression profile in the approach traces completely disappeared for poly(PMVE-A) (Fig. 2c, black curve) and was greatly reduced for poly(A-PMVE-A) (Fig. 2d, black curve). Moreover, in the vicinity of the glass surface, the AFM tips were found to 'snap-in' to the sample surface. This is ascribed to the attractive forces exerted between the surface and the collapsed polymer layer on the AFM probe. These observations prove that poly(PMVE-A) and poly(A-PMVE-A) polymers grafted on AFM tips undergo a conformational transition upon thermal stimulation. The related dehydration of the chains triggers phase separation, leading to a collapsed polymer layer that can no longer be compressed. When the tips are retracted from the surface, a large attractive peak shows up, typical for

adhesion between the relatively compact polymer layer on the tip and the glass surface (Fig 2c and 2d, red curves). The time needed to reach the collapsed state was very different for both PMVE systems. While poly(PMVE-A) collapsed rapidly after about 15 minutes, poly(A-PMVE-A) started to collapse after only one hour (see Table 1).

The reversible character of the collapsing behaviour was also studied. It is known that the different PMVE macromonomers exhibit a reversible phase separation in solution, regardless of their molecular weight or chain-end functionality.[16] After a heating step in water at 50 °C during one hour, AFM tips were immersed in water at room temperature and their behaviour was followed by force spectroscopy as a function of time. In practice, the onset of the compression profile was identified on each approach trace, at different immersion times at room temperature. The collected onset distances were compared to the ones corresponding to the completely swollen PMVE tips, providing a ratio that reflects the rate of recovery reached after a given time. As can be observed in Fig. 3, the tip grafted with poly(PMVE-A) exhibits a rather linear change of swelling ratio with time. Its transition back to the swollen state is complete after 3 hours. Interestingly, the poly(A-PMVE-A) tip recovers most of its low-temperature swollen state after only ten minutes.
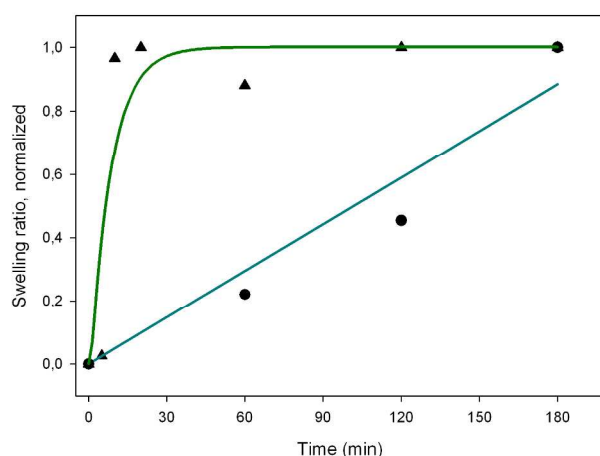

Fig. 3 Recovery rate of the swollen state as a function of time after heating the thermoresponsive AFM cantilevers above the LCST in water. Mono-acrylate PMVE tip (circle data points, blue line fit) and bis-acrylate PMVE tip (triangle data points, green line fit) exhibit dissimilar kinetic profiles. The swelling ratio is the ratio between the onset distances of the compression profiles measured at different immersion times at room temperature after a heating step at 50 °C and measured for the completely swollen brushes

We attribute the different kinetics of reswelling to the macromolecular architecture: the cross-linking of bis-acrylate PMVE limits the amplitude of shrinking when it is heated above the LCST, as evidenced by the remaining compression profile above the LCST (see above). The limited amplitude of shrinking is also confirmed by the AFM images below and above the LCST (see ESI). The occupied volume is thus higher than for the mono-acrylate version. The possibilities of attractive intramolecular segment-segments interactions are limited due to the constraints imposed by the cross-linking

points. Both types of PMVE tips are thus collapsed at different extents when heated at 50 °C, poly(A-PMVE-A) being less compact than the mono- acrylate PMVE system. Therefore, the recovery of the swollen state is faster for bis-acrylate PMVE.

Table 1 Collapse and reswelling times of PMVE acrylates grafted on AFM tips and on silicon substrates.

	Collapsing time	Reswelling time
PMVE-A on tip	15 min	3 h
PMVE-A on Si substrate	30 min	72 h
A-PMVE-A on tip	1 h	10 min
A-PMVE-A on Si substrate	4 h	20 min

The behaviour of the same PMVE-based polymers grafted on macroscopic silicon substrates was also investigated below and above the LCST. The same trends were observed (see Table 1) when we compare mono- and bis-acrylate PMVE, *i.e.* a longer collapsing time and shorter reswelling time for poly(A-PMVE-A). Interestingly, an increase of all the collapse and reswelling times was observed for these samples grafted on a macroscopic surface. This is especially the case for the poly(PMVE-A) sample: it took 72 hours to recover its low temperature state, compared to only 3 hours for the same chains grafted on an AFM tip. The explanation for the kinetics of this collapsing/reswelling phenomenon to be slowed down can be found in the constraints experienced by the polymer chains in the macroscopic sample. Indeed, the large flat surface implies a more compact and dense structure and thus more confinement of the polymer chains compared to a curved, nanoscale tip, and therefore less accessibility for the solvent molecules, as well as less mobility for the polymer chains. This is in agreement with previous theoretical studies, which had predicted that for curved surfaces a radius below 50 nm has a very pronounced effect on the volume available for each chain. The segment density is strongly reduced as compared to a flat surface.[26] Cooling down and swelling back a macroscopic polymer layer takes thus more time than what is needed for a grafted nano-sized AFM tip.

Conclusions

Mono-acrylate and bis-acrylate terminated PMVE chains were grafted onto AFM tips and macroscopic silicon substrates. AFM-based force spectroscopy experiments were then performed in order to characterise at the nanoscale the temperature dependent swelling/collapsing process and its reversibility on both substrates. We evidenced that the collapsing and reswelling ability of the grafted poly(PMVE) chains is very different for the two macromolecular architectures and the two substrates. The time needed to reach the collapsed state above the LCST was much shorter for poly(PMVE-A) than for poly(A-PMVE-A), the cross-linking of telechelic bis-acrylate PMVE limiting the amplitude of collapsing. The reversible character of the collapsing behaviour

was also studied and accordingly, the recovery of the swollen state is faster for bis-acrylate PMVE.

An increase of all the collapsing times was observed for the samples grafted on the macroscopic silicon surface. The reversible character and its kinetics are also much affected. For a same grafting density, the volume available for each chain is much higher on a curved surface with a radius of 20 nm, than for a flat substrate. The large flat surface implies more confinement of the polymer chains compared to a curved, nano-sized tip, and therefore less accessibility for the solvent molecules, as well as less mobility for the polymer chains.

Our results thus show that the collapsing and reswelling ability of thermoresponsive polymers attached to surfaces, as well as the reversible character of the transition and its dynamics, is potentially adjustable to target specific applications.

Experimental

Synthesis of the PMVE acrylic macromonomers

Cationic polymerisation of methyl vinyl ether (MVE) was performed in toluene at temperatures between -40 and -5°C in a reactor. The initiating system was a combination of 1,1-diethoxyethane (DEE) or 1,1,3,3-tetramethoxypropane (TMOP) with ZnI_2 as an activator, as described earlier.[30] The initiator was prepared *in situ* from DEE or TMOP and trimethylsilyl iodide, in toluene at -40°C. After condensation of an initial amount of MVE, the polymerisation was triggered by addition of ZnI_2. MVE was then continuously fed to the reactor at -5°C at a known feed rate until the desired monomer-to-initiator ratio was obtained. Active chains were end-functionalised by addition of a terminating agent, 2-hydroxyethyl acrylate. Data reported in Table 2 show that the cationic polymerisation was controlled: the experimental molecular weight was close to the theoretical molecular weight, with a low dispersity and the NMR peak integration confirmed that the experimental molecular weight was dictated by the monomer-to-initiator ratio.

Table 2 Macromolecular characteristics of PMVE macromonomers.

Samples	Macromonomers	M_n (th) (g.mol^{-1})	M_n (NMR) (g.mol^{-1})	M_n (SEC) [a] (g.mol^{-1})	Đ
1	PMVE-A	1000	1100	1100	1.08
2	A-PMVE-A	2000	2300	2000	1.18

[a] Measured by size-exclusion chromatography calibrated with PEO standards in THF.

Surface preparation

AFM tips, glass and silicon substrates were cleaned by UV-ozone treatment for 15 minutes (UV-ozone cleaner, Model 42, Jelight Company Inc.) and then rinsed with ethanol.

Electrografting on AFM tips

Briefly, the electro-initiated polymerisation was carried out in a one-compartment cell equipped with a Pt counter-electrode and a Pt pseudo-reference (the working electrode being the cantilever chip) placed in a glovebox under a dry inert atmosphere. The macromonomer was dissolved in dried DMF containing tetraethylammonium perchlorate (5.10^{-2} mol.L^{-1}) as conducting salt. The experiments were performed using an EG&G potentiostat/galvanostat (M273), following our previously published procedure.[24] Sweeps between the initial potential and the potential at the top of the grafting peak were realised. Sweeps were stopped at the grafting peak, thus before the second reduction peak corresponding to the reduction of the macromonomer in solution (and thus the formation of a polymer in solution) appeared. We used silicon nitride cantilevers with a nominal spring constant of 0.05 N.m^{-1} and tip radius of 20 nm (MLCT series, Bruker).

AFM: Force curves measurement and analysis

The AFM experiments were performed with a PicoPlus 5500 microscope (Agilent Technologies, Inc.). MLCT cantilever tips (Bruker) were used, with nominal spring constant of 0.05 N.m^{-1} and tip radius of 20 nm. Cantilevers spring constants were calibrated after experiment by the thermal noise method. Upon approaching tip and glass substrate, a threshold loading force was set at 500 pN. During the contact, the polymer chains can physisorb onto the opposite surface and bridge the substrate and the tip. When moving the tip away from the substrate, the bridging molecules are stretched. Approach-retraction curves were performed in MilliQ water (Millipore) at a typical velocity of 300 nm.s^{-1}.

The shapes of both the approach and retraction traces were carefully analysed, especially near the contact region, to detect the compression profile, which provides information on the swollen or precipitated states. The onset of the compression profile corresponds to the distance where the signal on the approach curve starts to deviate from the baseline.

Acknowledgements

Notes and references

[a] Nanochemistry and Molecular Systems, Department of Chemistry, University of Liège, Sart-Tilman B6a, 4000 Liège, Belgium. Tel: +32 4 3665991; E-mail: nwillet@ulg.ac.be ; asduwez@ulg.ac.be
[b] Center for Education and Research on Macromolecules, Department of Chemistry, University of Liège, Sart-Tilman B6a, 4000 Liège, Belgium. Tel: +32 4 3663491; E-mail: c.jerome@ulg.ac.be
[c] Polymer Chemistry Research Group, Department of Organic Chemistry, Ghent University, Krijgslaan 281 S4, B-9000 Ghent, Belgium.

References

1. N. Willet, J. F. Gohy, L. Auvray, S. Varshney, R. Jerome and B. Leyh, *Langmuir*, 2008, **24**, 3009-3015.
2. Z. Li, E. Kesselman, Y. Talmon, M. A. Hillmyer and T. P. Lodge, *Science*, 2004, **306**, 98-101.
3. J.-F. Gohy, N. Willet, S. Varshney, J.-X. Zhang and R. Jerome, *Angew. Chem. Int. Ed.*, 2001, **40**, 3214-3216.
4. S. Lecommandoux, O. Sandre, F. Checot, J. Rodriguez-Hernandez and R. Perzynski, *Adv. Mater.*, 2005, **17**, 712-718.
5. F. Checot, J. Rodriguez-Hernandez, Y. Gnanou and S. Lecommandoux, *Biomolecular Engineering*, 2007, **24**, 81-85.
6. N. Willet, J. F. Gohy, L. C. Lei, M. Heinrich, L. Auvray, S. Varshney, R. Jerome and B. Leyh, *Angew. Chem.-Int. Edit.*, 2007, **46**, 7988-7992.
7. M. Ikeda, T. Tanida, T. Yoshii and I. Hamachi, *Adv. Mater.*, 2011, **23**, 2819-2822.
8. W. Lequieu, N. I. Shtanko and F. E. Du Prez, *Journal of Membrane Science*, 2005, **256**, 64-71.
9. I. Tokarev, V. Gopishetty, J. Zhou, M. Pita, M. Motornov, E. Katz and S. Minko, *ACS Applied Materials & Interfaces*, 2009, **1**, 532-536.
10. W. Van Camp, F. E. Du Prez, H. Alem, S. Demoustier-Champagne, N. Willet, G. Grancharov and A.-S. Duwez, *Eur. Polym. J.*, 2010, **46**, 195-201.
11. Y. Roiter, I. Minko, D. Nykypanchuk, I. Tokarev and S. Minko, *Nanoscale*, 2012, **4**, 284-292.
12. L. Dai, *Intelligent Macromolecules for Smart Devices: From Materials Synthesis to Device Applications*, Springer-Verlag, London, 2004.
13. D. M. Jones, J. R. Smith, W. T. S. Huck and C. Alexander, *Adv. Mater.*, 2002, **14**, 1130-1134.
14. Y. E. Kirsh, *Water Soluble Poly-N-Vinylamides: Synthesis and Physicochemical Properties*, 1998.
15. S. Verbrugghe, K. Bernaerts and F. E. Du Prez, *Macromol. Chem. Phys.*, 2003, **204**, 1217-1225.
16. V. Aseyev, S. Hietala, A. Laukkanen, M. Nuopponen, O. Confortini, F. E. Du Prez and H. Tenhu, *Polymer*, 2005, **46**, 7118-7131.
17. J.-F. Lutz, O. Akdemir and A. Hoth, *J. Am. Chem. Soc.*, 2006, **128**, 13046-13047.
18. Z.-B. Hu, T. Cai and C.-L. Chi, *Soft Matter*, 2010, **6**, 2115-2123.
19. B. Verdonck, E. J. Goethals and F. E. Du Prez, *Macromol. Chem. Phys.*, 2003, **204**, 2090-2098.
20. K.-F. Arndt, T. Schmidt and R. Reichelt, *Polymer*, 2001, **42**, 6785-6791.
21. S. Minko, *Journal of Macromolecular Science, Part C*, 2006, **46**, 397-420.
22. E. J. Goethals and F. Du Prez, *Prog. Polym. Sci.*, 2007, **32**, 220-246.
23. S. Gabriel, P. Dubruel, E. Schacht, A. M. Jonas, B. Gilbert, R. Jérôme and C. Jérôme, *Angew. Chem. Int. Ed.*, 2005, **44**, 5505-5509.
24. S. Gabriel, C. Jerome, R. Jerome, C.-A. Fustin, A. Pallandre, J. Plain, A. M. Jonas and A.-S. Duwez, *J. Am. Chem. Soc.*, 2007, **129**, 8410-8411.
25. S. Cuenot, S. Gabriel, R. Jerome, C. Jerome, C.-A. Fustin, A. M. Jonas and A.-S. Duwez, *Macromolecules*, 2006, **39**, 8428-8433.
26. I. Szleifer and M. Carignano, in *Polymeric Systems*, eds. I. Prigogine and S. A. Rice, Wiley, 1996, vol. 94, pp. 165-260.
27. H.-J. Butt, M. Kappl, H. Mueller, R. Raiteri, W. Meyer and J. Rühe, *Langmuir*, 1999, **15**, 2559-2565.
28. J. N. Israelachvili, *Intermolecular And Surface Forces*, Academic Press, 2010.
29. H. J. Taunton, C. Toprakcioglu, L. J. Fetters and J. Klein, *Nature*, 1988, **332**, 712-714.
30. N. H. Haucourt, E. J. Goethals, M. Schappacher and A. Deffieux, *Die Makromolekulare Chemie, Rapid Communications*, 1992, **13**, 329-336.