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Polymer-functionalised Polymer Nanoparticles and their Behaviour in Suspensions

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Soft polymer nanoparticles can be functionalised with end-tethered polymer chains to control their solvent compatibility and stability. Controlling and understanding the behaviour of such functionalised latex suspensions is critical for their comprehensive applications. To investigate the effect of the nanoparticles architecture on their rheological behaviour, a library of polystyrene nanoparticles functionalised with a canopy of end-tethered poly(methyl acrylate) chains with different degrees of polymerisation and grafting densities was prepared. When the end-tethered polymer chains were long enough, the suspensions of polymer-functionalised nanoparticles underwent a liquid to gel transition when the concentration of nanoparticles was increased. The architecture of the polymer canopy was the determining factor for the mechanical properties of the resulting gels, nanoparticles with moderate grafting density where the polymer chains adopt a relax polymer brush conformation led to the formation of the strongest and most robust gels. In comparison to suspensions made with polymer functionalised nanoparticles particles with a soft and swollen core formed gels with higher yield stress at lower solid content.

Introduction

Nanoparticles (NPs) with a grafted layer of polymers have become ubiquitous building blocks for applications from the biomedical field to the production of sustainable energy. In those systems, end-tethered polymer chains are often used to modify the properties of NPs such as stability, solvent compatibility, dispersibility, and assembly. Polymer chains tethered to a latex nanoparticles represent a particular challenge since both the canopy of end-tethered chains and the core of the nanoparticles are soft and deformable. Thus, designing the ideal polymer layer to optimize the behavior of the NPs for a specific application is non-trivial and new design principles are needed to rationally engineer such polymer canopy. Polymer NPs functionalised with a canopy made of end-tethered polymer chains combine the complex rheological behavior of polymer chains and polymer colloids. Furthermore, to facilitate the processing of such materials, it is essential to understand how the architecture of such particles influences their behavior in flow.

Polymer solutions can be complex non-Newtonian viscoelastic fluids, especially in the semi-dilute and concentrated regime, when the concentration of polymer in solution is above the critical overlap concentration. The behavior of the polymer chains in solution does not only depend on the concentration but also on the architecture, topology, and flexibility of the chains. Branched polymers, such as star-, H-, or comb-shaped macromolecules, exhibit larger shear viscosities than their linear analogs. The viscosity of solutions of branched polymers increases as the number of branches increases, while the effect of the branch length become more marginal as the number of arms increases. One of the key features of branched systems is the restricted arm interpenetration and arm entanglement as the branching degree increases. In comparison to solutions of linear polymer chains, the overlap concentration of solutions of dendrimers and polymers with a branched architecture occurs at higher concentrations because of the limited effective chain entanglement. In comparison to polymer solutions, the rheological behavior of colloidal dispersions is controlled by even more factors; the viscoelasticity depends not only on the volume fraction occupied by the colloids and on the colloid-colloid interaction, but is also affected by the effects on the local flow patterns of the reorganization and reorientation of the particles in suspension and the formation (or destruction) of colloidal mesostructures. Furthermore, when dealing with soft and deformable colloids in suspension, both the shape and the volume occupied by the particles can change under the application of shear, leading to strong flow-dependent behavior. The softness of the nanoparticles affects the mechanical properties of the resulting gels and glasses and the concentration needed to observed a liquid to gel transition. Soft and deformable particles are expected to form stronger gels than hard spheres. The behavior of nanoparticles in suspension could be tuned by the functionalization of the surface of the nanoparticles with a
canopy of end-tethered polymer chains. The behavior of such nanoparticles dispersed in a polymer matrix has been shown to depend on composition of the canopy as determined by the degree of polymerization (N) and grafting density (σ) of the chains since those parameters influence both the particle/particle interaction and the particle/environment interaction. The influence of N and σ on the stability of polymer functionalized nanoparticles dispersed in a solvent or in a solid matrix has been widely studied for nanoparticles with a rigid core. In such systems, the dynamics of the nanoparticles suspensions and the particle/particle interactions in suspension were mostly governed by the architecture of the polymer canopy via the excluded volume interactions and chain configuration entropy, and fluctuations of polymer canopy influenced the fragility of the particle assemblies. Furthermore, for similar polymer canopy, the degree of swelling of the polymer canopy change the chain conformation in the canopy and the resulting behavior of the suspensions. The behavior of such nanoparticles dispersed in a polymer matrix has been shown to depend on composition of the canopy as determined by the degree of polymerization (N) and grafting density (σ) of the chains since those parameters influence both the particle/particle interaction and the particle/environment interaction. The influence of N and σ on the stability of polymer functionalized nanoparticles dispersed in a solvent or in a solid matrix has been widely studied for nanoparticles with a rigid core. In such systems, the dynamics of the nanoparticles suspensions and the particle/particle interactions in suspension were mostly governed by the architecture of the polymer canopy via the excluded volume interactions and chain configuration entropy, and fluctuations of polymer canopy influenced the fragility of the particle assemblies. Furthermore, for similar polymer canopy, the degree of swelling of the polymer canopy change the chain conformation in the canopy and the resulting behavior of the suspensions.

Here, to understand the relation between the rheological and mechanical properties of suspension and the structure of soft-core/soft-corona polymer nanoparticles dispersed in a good solvent, we designed a library of soft and swollen crosslinked polystyrene (PS) nanoparticles functionalized with a canopy of end-tethered poly(methyl acrylate) (PMA) chains. Using surface-initiated atom transfer radical polymerization (SI-ATRP) the length of the polymer chains was precisely controlled, and the grafting density was tuned during the synthesis of the PS core. The rheological properties of suspensions of these PS@PMA NPs in different solvents were investigated to get insights on how the architecture of the canopy of end-tethered polymer chains and how the combination of a swollen gel core with swollen polymer canopy affects the NPs suspension.

Experimental

Synthesis of polystyrene nanoparticles core (PS-SS-Br)

First, 6.5 mL of styrene (St, 1 eq), 82 µL of divinylbenzene (DVB, 0.01 eq) and 0.65 mL of hexadecane (HD, 0.04 eq) were mixed with 0.0552 g of 2,2′-azobis(2-methylbutyronitrile) initiator (V-59, 0.01 eq). Then, 48 mL of sodium dodecyl sulfate (SDS) solution (10 mM) was added and the mixture was pre-emulsified for 15 min by magnetic stirring at 600 rpm. The solution was sonicated for 2 min (20 kHz, 70% A, 10 s on / 2 s off) to obtain a miniemulsion before being transferred to a round bottom flask and heated to 80 °C. After 2.5 h of polymerization, 4 mL of a 250 mM solution of SDS was added and the system was purged by bubbling Ar for 10 min. Then, to create a thin layer of inimer (MA-SS-Br, figure S1, SI) containing polymer network at the surface of the nanoparticle, a mixture of 89-98 mol% of St (1.33 mL), 1 mol% DVB (16.6 µL), 1-10 mol% of MA-SS-Br (0.0326-0.326 mL) and V-59 (0.0115 g) was subsequently added dropwise with a syringe pump at a rate of 1 mL/h. The reaction mixture was left stirring overnight before being filtered. The PS particles in aqueous suspension were then precipitated in 200 mL of MeOH and air-dried. To completely eliminate HD and SDS from the PS nanoparticles, the NPs were dispersed in THF and precipitated in MeOH three times. Finally, the NPs were air-dried.

To determine the number of initiating sites at the surface of the NP, the sulfur content in the NPs was analyzed. The NPs were dispersed in water and stabilized with cetyltrimethyl ammonium chloride (CTAC). A PS-SS-Br NPs suspension in DCM was added dropwise to 10 mL of an aqueous solution containing 5.0 mg of CTAC and sonicated. Then, the DCM was
evaporated under mild vacuum (200 mbar, 40 °C). The sulfur content in the resulting aqueous suspension of PS NPs was measured by inductive coupled plasma atomic emission spectrometry (ICP-AES) with an ACTIVA M spectrometer (Horiba Jobin Yvon) equipped with a Meinhardt-type nebulizer and a cyclone chamber, and processed with ACTIVAnalyst 5.4.

Synthesis of the end-tethered canopy of poly(methyl acrylate) on the surface of the PS core (PS@PMA)

In a typical reaction, 0.4 mL of methyl acrylate, 0.1 mL of a solution containing Cu(II)Br₂ (2000 ppm) and PMDETA (Cu(II):ligand = 1:10 molar ratio) in DMF were added to a vial containing to a suspension of 50 mg PS-SS-Br NPs dispersed in 4 mL of anisole. PDMS (0.1 mL) was added to the suspension. The mixture was stirred and purged with argon for 30 min. Then, 0.5 mL solution of ascorbic acid (1600 ppm) in DMF was added. This resulting suspension was degassed with argon for another 10 min, and the vial was then placed into an oil bath at 60 °C and let to react. Once the appropriate conversion was reached, the reaction mixture was diluted with THF, precipitated in MeOH and dried overnight under vacuum. The reaction was repeated with varying amounts of monomer, Cu(II)/ligand and bromoisobutyrate grafted moieties.

To characterize the end-tethered PMA (Figure 1), the chains were cleaved from the PS@PMA NPs. The disulfide bonds between the polystyrene core and the PMA chains were cleaved by a reduction with dithiothreitol. A suspension of PS@PMA NPs was prepared by mixing 0.1g of PS@PMA NPs with 10 mL of DCM for 24 h. Then, DL-dithiothreitol (DTT, 10 mg) and two drops of 1,8-diazabicyclo[5.4.0]inden-7-ene (ca. 20 mg) were added to the NP suspension and stirred for 24 h. After evaporation of the solvent, the dried and cleaved polymer/particle mixture was mixed in 10 mL of THF with an additional 5 mg of DTT and stirred overnight. The suspension was then filtered through a syringe filter (PTFE, Ø=0.2 µm). The solutions were centrifuged at 29068 g for 20 min to eliminate the residual PS core and then, the molecular weight of PMA in solution was measured by SEC in THF.

Rheological behaviour of PS@PMA suspensions

Suspensions of PS and PS@PMA NPs and solution of free PMA (Mₙ, 40k) of 0.5% were prepared in anisole at a concentration ranging from 0.1 to 15 wt%. The rheological properties of the suspensions were measured with a Bohlin Gemini 200 rotational rheometer at 25 °C equipped with a cone and plate geometry of 40 mm of diameter and 4° of cone angle. The gap was set at 150 µm. Continuous shear experiments were realised by varying the shear rate between 0.1-1000 s⁻¹. The dynamic behaviour of the suspensions was studied in oscillatory shear experiments; for frequency-sweep experiments, the strain applied to the system was fixed to 10% and from the frequency varied from 0.1 to 100 rad/s and in strain-sweep experiments, the frequency was fixed to 10 rad/s and the strain varied from 0.1 to 1000%.

Results and discussion

A library of core-corona nanoparticles with a core of polystyrene grafted with a canopy of poly(methyl acrylate) chains (PSₙ@PMAₙ) with different chain length (N) and grafting density (α) was prepared (Table 1). The synthesis of the particles proceeded via a three-step process. First, miniemulsion polymerization was used to prepare polystyrene nuclei used to make core-shell nanoparticles through a starved-fed emulsion polymerization process to create a thin layer of a copolymer of styrene and the imimer at the surface of the polystyrene nanoparticle. The grafting density was tuned by controlling the concentration of imimer in the outer layer of the polystyrene core. Finally, each imimer was used to initiate the polymerization of methyl acrylate by surface-initiated atom transfer radical polymerization (SI-ATRP). In the dry state, at room temperature, the resulting NPs were composed of a rigid glassy core surrounded by a soft rubbbery corona (Figure 1c). PS and PMA were selected because they are strongly immiscible (γ_{PS/PMA} = 0.03 N=169 γ_{PS/PMA} ) as observed experimentally with binary mixtures of PS and PMA and PS/PMA block copolymer readily undergoing phase segregation in order to prevent any type of specific interaction between the PS core and the PMA canopy. Furthermore, using SI-ATRP to grow the PMA from the surface allowed to precisely tune the length of the grafted chains, since the polymerization of the methyl acrylate was controlled as demonstrated by the linear increase of monomer conversions with the polymerization time (Figure S2, SI). The experimental molecular weights of the PMA brushes determined by SEC (Mₙ,SEC) were in good agreement with the expected values based on the monomer conversion measured by NMR spectroscopy and the number of initiating sites measured by ICP (Table S2, SI). The amount of PS and PMA in the NPs could be controlled by the architecture of the PMA canopy and the chemical composition of the NPs was quantified by FTIR spectroscopy using a calibration made of a binary mixture of pure PS NPs and linear PMA in known weight ratios (Figure S3, SI). The contents of PMA in each sample scaled as expected with the different α and N (Figure 2a). The combined analysis of the particles by ICP, GPC, NMR and FTIR spectroscopy showed that the length and the grafting density of the PMA chains in the PS@PMA NPs were precisely controlled which allowed for the tuning of the architecture of the PMA canopy. The PS@PMA NPs with their well-defined composition were used to investigate the effect of the NP architecture on the behavior of their resulting suspensions. The thickness of the canopy of PMA was dependent on the solvent quality and decreased when the solvent quality becomes poorer. In water, a poor solvent for both PS and PMA (Table S1, SI), both the PS and the PMA were shrunk, and the variation in diameter with increasing the N of PMA was limited (Table S2, SI). In anisole, a good solvent for both PS and PMA, and in DMSO, poor solvent for PS but a good solvent for PMA (Table S1, SI), the PS@PMA NPs swelled and a variation of the thickness of the canopy with its architecture was observed.
When pure PS NPs were dispersed in anisole, they experienced a swelling of ca. 100 %, while when the same NPs were dispersed in DMSO they only experience a swelling of less than 15 % (Table S2, SI). PS@PMA NPs were dispersed in the same solvents and the difference in the size of the swollen PS@PMA NPs were compared to the size of the pure PS NPs in the same solvent to calculate the thickness of the PMA canopy. At low grafting density, only a marginal increase in diameter was observed because the canopy of PMA was collapsed on the surface and occupied a limited volume (Figure 2 and Table S2, SI). At higher σ, an increase in the diameter of the NP was observed in water due to the crowding of neighboring polymer chains forcing the PMA to adopt a stretched conformation.

### Table 1. Library of PS@PMA nanoparticles

| Sample                  | Reaction Time (h) | $M_g$ PMA (10^4 g/mol) | $N$   | Grafting density $σ$ (nm²) |
|-------------------------|-------------------|------------------------|-------|---------------------------|
| PS$_{20}$@PMA$_{200}$   | 0.5               | 3.1                    | 36    | 2.5                       |
| PS$_{20}$@PMA$_{200}$   | 1                 | 6.0                    | 70    | 2.5                       |
| PS$_{20}$@PMA$_{200}$   | 2                 | 10.0                   | 128   | 2.5                       |
| PS$_{20}$@PMA$_{200}$   | 2.5               | 15.0                   | 171   | 2.5                       |
| PS$_{20}$@PMA$_{200}$   | 3                 | 19.0                   | 220   | 2.5                       |
| PS$_{20}$@PMA$_{200}$   | 1                 | 35.0                   | 406   | 2.5                       |
| PS$_{20}$@PMA$_{200}$   | 3                 | 42.0                   | 493   | 2.5                       |
| PS$_{20}$@PMA$_{200}$   | 6                 | 54.0                   | 623   | 2.5                       |
| PS$_{20}$@PMA$_{200}$   | 0.5               | 2.6                    | 31    | 0.80                      |
| PS$_{20}$@PMA$_{200}$   | 0.5               | 6.9                    | 79    | 0.80                      |
| PS$_{20}$@PMA$_{200}$   | 2                 | 20.0                   | 228   | 0.80                      |
| PS$_{20}$@PMA$_{200}$   | 2                 | 30.0                   | 349   | 0.80                      |
| PS$_{20}$@PMA$_{200}$   | 3                 | 42.0                   | 493   | 0.80                      |
| PS$_{20}$@PMA$_{200}$   | 4.5               | 51.0                   | 593   | 0.80                      |
| PS$_{20}$@PMA$_{200}$   | 0.5               | 3.8                    | 44    | 0.17                      |
| PS$_{20}$@PMA$_{200}$   | 1                 | 8.5                    | 99    | 0.17                      |
| PS$_{20}$@PMA$_{200}$   | 2                 | 23.0                   | 267   | 0.17                      |
| PS$_{20}$@PMA$_{200}$   | 1.5               | 32.0                   | 377   | 0.17                      |
| PS$_{20}$@PMA$_{200}$   | 2                 | 41.0                   | 474   | 0.17                      |
| PS$_{20}$@PMA$_{200}$   | 2.5               | 52.0                   | 610   | 0.17                      |

The thickness of the layer of tethered polymer chains on a substrate varies with $N$, the repulsion between the monomers, the solvent type, $σ$ and blob size. When the substrate is the curved surface of a NP the behavior of the end-tethered chains is more complex than on a flat substrate due to the curvature dependence of the polymer chains conformation since the local polymer concentration decreased with increasing distance from the surface of the NPs. Here, the solvated radius of the NPs was used to calculate the thickness of the PMA corona (Figure 2B). The correlation between the thickness of the brush layer ($T$) and $N$ in various solvents, scale with:

$$T \sim k(N)^α$$  \hspace{1cm} (eq 1)

where $α$ is the stretching parameter of the polymer chain, with $α = 0$ for completely collapsed corona chains on the surface and $α = 1$ for completely stretched chains, the value of the scaling exponent $α$ is a function of grafting density and solvent quality. According to the extended Daoud-Cotton model and modelization and self-consistent field theory, in a good solvent, under semi-diluted grafting conditions, the thickness of the polymer brushes scale with $N^{3/5}$ while at high grafting density the thickness of the brush layer should scale linearly with $N$.  

The results of the fit of eq. 1 to the thickness of the PMA canopy (Table S3, SI) show that in anisole and in DMSO, $σ$ increased as $σ$ increased due to the steric constraints of tethered polymers chains. At a high grafting density, the variation in the thickness of the PMA canopy suggested that due to a high local polymer concentration and high solvent quality, the brushes adopted a stretched conformation. For NPs with moderate grafting density, the brushes were extended, but not fully stretched, indicative of the semi-dilute brush regime. For samples with low $σ$, the polymer brushes adopted a more collapsed conformation. When the NPs were dispersed in water, no clear trend in the variation of the thickness of the PMA canopy with $N$ and $σ$ could be observed. The effect of $N$ and $σ$ on the thickness of the PMA canopy suggest that, in anisole, the tethered chains were forced to adopt a stretched conformation on the surface of NPs with high and medium $σ$ due to the steric hindrance, while at lower $σ$ the tethered chain adopted a more relaxed conformation.
The behavior of the suspension of PS@PMA NPs, naked PS NPs and a binary mixture of PS NPs and free PMA\textsubscript{40k} in anisole was investigated under continuous shear. A solution of free PMA\textsubscript{40k} chains and the binary mixture of PS NPs and PMA\textsubscript{40k} chains displayed a mostly Newtonian behavior (Figure 3a) because of the limited interaction and entanglements in those systems. In contrast, suspensions of PS NPs and PS@PMA NPs exhibited a shear thinning behavior attributed to the presence of highly swollen PS or PS@PMA in anisole leading to the formation of either jammed suspensions or interdigitated networks.\textsuperscript{18, 45}

Figure 3. (a) Dynamic viscosity of 10 wt% suspension PS@PMA in anisole and (b) effect of NPs concentration of the zero-shear viscosity of suspensions of (•) PS NPs, (△) PS\textsubscript{h}@PMA\textsubscript{40k} NPs, (●) free PMA\textsubscript{40k} and (○) a binary mixture of PS NPs and free PMA\textsubscript{40k}.

The zero-shear viscosity ($\eta_0$) obtained for the suspensions prepared with the different NPs systematically increased with increasing the concentration of NPs in suspension (Figure 3b). The viscosity of the suspensions at a given concentration increase with increasing N. However, the effect of $\sigma$ was as straightforward (Figure S6); for 10 wt% suspensions of NPs with relatively long brushes ($N \approx 500$), the viscosity of high and medium grafting density samples were similar but larger than for samples with the lowest grafting density. The influence of the architecture of the PMA canopy was especially evident when comparing suspension containing the same concentration of NPs in number (or polystyrene core) (Figure S7b) for the same number of NPs in suspension, $\eta_0$ increased with $\sigma$, while the influence of the architecture was less critical when comparing suspensions containing the same amount of methyl acrylate (Figure S7c).

The transition between the dilute and semi-diluted regime ($C'$) was defined as the inflection point in the variation of $\eta_0$ with NP concentration (Figure 3b).\textsuperscript{22} The $C'$ of PS suspension, caused by space jamming, was ca. 6wt%. and the $C'$ of PS@PMA NPs decreased with increasing $N$ and $\sigma$ of the PMA chains (Figure 4). In comparison to PS NPs, PS@PMA NPs could, in addition to space jamming, also undergo interpenetration of the PMA canopy and entanglement of the PMA chains can occur for the chains with larger $N$, leading to an increase in viscosity. However, the addition of free PMA chains decreased the viscosity of the suspension (Figure 3).
Figure 4 shows that the concentration of NPs in suspension required to observe the transition between the dilute and semi-dilute regime decreased with increasing polymer on the NP was the key factor influencing $[NP]'$, and a decrease in $[NP]'$ was observed. However, the total amount of polymer on the NP was the key factor influencing $[NP]'$, and similar effect on $[NP]'$ were observed for NPs with few long PMA chains or multiple short PMA chains, an increase in either $N$ or $\sigma$ promoting the NP-NP interactions and reducing the number of NPs needed to achieve the same effect of the flow behavior of the suspensions.

When the concentration of the PS@PMA increased above $C^*$, a transition between a liquid-like state and a gel-like state was observed for some NP architectures (Figure 5). Concentrated suspension of PS NPs formed gels at a concentration superior to ca. 8 wt%, while suspensions of PS@PMA NPs with long chains ($N > 200$ units) formed gels at concentrations ranging from 2 to 15 wt%. However, suspensions of PS@PMA NPs with short chains ($N < 175$ units) did not form gels even at concentrations as high as 20 wt%. Similarly, binary mixtures of PS NPs and free PMA chains did not form gel-like suspension even at high concentrations.

Figure 5B shows that at 10 wt% in anisole, solutions of free PMA and binary mixtures of PS NPs and free PMA displayed a viscous behavior while concentrated suspensions of pure PS NPs and of grafted PS@PMA behaved as viscoelastic solids ($G' > G''$). Furthermore, gels formed with pure PS NPs displayed a lower yield strain than the gels made of PS@PMA NPs. While PS@PMA NPs formed viscoelastic solids, the binary mixture of PS NPs and free PMA, with the same chemical composition, did not. The formation of colloidal gels with PS NPs suspension could only be ascribed to core-core interactions and jamming, the addition of free PMA chains to the PS core were much longer than the critical entanglement length ($N_{\text{e},\text{PMA}} = 125$) of PMA, the interpenetration, and potential entanglement, of the PMA canopies led to the formation of a network of PS@PMA NPs, where the PS core in PS@PMA NPs acted as junction points. In addition to anisole, a good solvent for both the PS core and the PMA canopy, suspension of PS@PMA were also prepared in DMso a selective solvent for the PMA. When the same nanoparticles were dispersed in DMso and in anisole at the same concentration (Figure 5c), the suspension in anisole systematically displayed a more solid-like behaviour and a larger complex viscosity than suspensions in DMso. Even when taking into account the volumes occupied by the NPs in the different solvent (Figure S10, SI), only weak gels were formed in DMso although the polymer canopy where similarly swollen in both solvent (Figure 2, Table S3). The swelling of the core in anisole in comparison to DMso was the only variable parameter and the easier gelation in anisole must be ascribed to an interplay between the PS core and the PMA canopy.

The interpenetration of the PMA canopy led to an earlier onset of the transition between the viscoelastic regimes. The rheological behavior of the suspensions, at any given $N$ and $\sigma$, was mainly influenced by the methyl acrylate content in suspension (Figure S8, SI), the observed $C'$ decreased linearly with the number of methyl acrylate units decorating the PS core. This was further evidenced when the concentration of $C'$ was calculated in terms of the number of NPs in suspension ([NP]$'$ in Figure S8c, SI). In this case, as both $N$ and $\sigma$ increased, a decrease in [NP]$'$ was observed. However, the total amount of polymer on the NP was the key factor influencing [NP]$'$, and similar effect on [NP]$'$ were observed for NPs with few long PMA chains or multiple short PMA chains, an increase in either $N$ or $\sigma$ promoting the NP-NP interactions and reducing the number of NPs needed to achieve the same effect of the flow behavior of the suspensions.

The effect of the architecture of the PMA canopy on the NPs concentration at the transition between the dilute and semi-dilute regime for suspension of PS@PMA in anisole. (a) Effect of the PMA chain length for PS@PMA$_{x}$ ($\bullet$) and PS NPs ($\blacksquare$), and (b) effect of grafting density for (●) PS@PMA$_{6k}$, (◆) PS@PMA$_{20k}$ and (◆) PS@PMA$_{40k}$.

Figure 4 shows that the concentration of NPs in suspension required to observe the transition between the dilute and semi-dilute regime decreased with increasing $N$ and increasing $\sigma$. The interpenetration of the PMA canopy led to an earlier onset of the transition between the viscoelastic regimes. The rheological behavior of the suspensions, at any given $N$ and $\sigma$, was mainly influenced by the methyl acrylate content in suspension (Figure S8, SI), the observed $C'$ decreased linearly with the number of methyl acrylate units decorating the PS core. This was further evidenced when the concentration of $C'$ was calculated in terms of the number of NPs in suspension ([NP]$'$ in Figure S8c, SI). In this case, as both $N$ and $\sigma$ increased, a decrease in [NP]$'$ was observed. However, the total amount of polymer on the NP was the key factor influencing [NP]$'$, and similar effect on [NP]$'$ were observed for NPs with few long PMA chains or multiple short PMA chains, an increase in either $N$ or $\sigma$ promoting the NP-NP interactions and reducing the number of NPs needed to achieve the same effect of the flow behavior of the suspensions.

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Figure 5. Formation of colloidal gels in concentrated suspensions of PS@PMA NPs. (a) influence of NP concentration (PS$_m$@PMA$_{40k}$) and architecture of the PMA canopy (PS$_x$@PMA$_{40k}$ and PS$_{20k}$@PMA$_{10k}$). (b) Elastic (solid symbol) and viscous (open symbol) moduli of 10 wt% suspension of (■) PS NPs, (▲)PS$_h$@PMA$_{40k}$ NPs, (●) free PMA$_{40k}$ and (◆) a binary mixture of PS NPs and free PMA$_{40k}$. (c) Complex viscosity of 10 wt% suspension of (■) PS NPs, (▲)PS$_h$@PMA$_{40k}$ NPs, and (★)PS$_m$@PMA$_{40k}$ NPs in anisole (filled symbol) and DMSO (open symbol).

Both the modulus and the yield strain of the PS@PMA NPs suspensions were affected by the architecture of the PMA canopy. Figure 6A shows that, at a fixed σ, as N of the canopy increased, the modulus of 10 wt% suspension increased and the behavior of the suspensions transitioned from liquid-like to gel-like. This transition was observed at a concentration much lower than with hard nanoparticles functionalized with polymer chains. This was even more directly observed by comparing the mechanical properties of PS@PMA NPs in suspension in anisole producing suspension of soft core surrounded by a soft canopy and the suspension in DMSO where a hard core is functionalized with the same polymer canopy (Figure S10). The suspensions in anisole of PS@PMA NPs functionalized with short PMA chains (N<150 units) did not form gels in the concentration range studied. The stiffness of the suspension, defined as $G^*$ ($G'$ + i$G''$) in the low strain regime, increased as a function of N (Figure 7, Figure S9, SI). However, when the chain length was kept constant and σ increased (Figure 6B) the properties of the colloidal gels prepared with the NPs varied in a more complex manner. For gels prepared with 10wt% of PS@PMA NPs having short brushes (N ca. 225 units) the gels prepared with the NPs with medium σ were the stiffest (higher $G^*$) and strongest (higher yield strain). No gelation was observed with the PS@PMA NPs having the highest σ at this brush length. However, for NPs having longer PMA chains (N ca. 500 units) all the different grafting density lead to the formation of gels (Figure S10, SI) and the gels prepared with the lowest grafting density were both the weakest and the most fragile, the gels prepared with NPs having the highest σ showed the highest yield strain, and those prepared with the NPs having medium σ were the strongest. Those results show that high σ can prevent the efficient interdigitation of the PMA canopy and the resulting effective NP-NP interactions due to the large the local PMA concentration in the canopies with high σ. Increasing the length of the polymer brush alleviated this effect likely because the effective local concentration of polymer decreased as the distance between the surface of the PS core and the surface of the PMA canopy increased.
Figure 6. Visco-elastic behavior ($G'$ (solid symbol) and $G''$ (open symbol)) of 10 wt% suspension of PS@PMA in anisole (i) and DMSO (ii). (a) Effect of PMA brush length for ($\bullet$) PS$_h@$PMA$_{10k}$, ($\Delta$) PS$_h@$PMA$_{20k}$, ($\blacktriangle$) PS$_h@$PMA$_{30k}$, and ($\blacktriangledown$) PS$_h@$PMA$_{40k}$. (b) Effect of grafting density with ($\bullet$) PS$_m@$PMA$_{20k}$, ($\blacklozenge$) PS$_m@$PMA$_{20k}$, and ($\blacktriangle$) PS$_l@$PMA$_{20k}$.

Figure 7 shows that the gelation of PS@PMA NPs with longer PMA chains, for which interdigitation of the PMA canopy was favored, led to an increase in the cohesion of the network formed. Yet, increasing the grafting density over a certain point decreased the efficiency of the canopy interdigitation. However, when the gels were prepared with a constant number of NPs in concentration (Figure S11), an increase in $N$ and $\sigma$ both led to an increase in the modulus and the yield strain of the colloidal gels. The mechanical properties of the colloidal gels suggested that both the number of PS cores acting as either a crosslinking point or a filler in the polymer network and the fraction of PMA in the samples and thus the canopy interdigitation were critical in determining the final behavior of the suspension.

At a constant mass fraction of NPs, suspensions of PS@PMA NPs in anisole were systemically stiffer and tougher than suspensions of the same NPs in DMSO. While the canopies of the PS@PMA NPs were undergoing similar swelling in both solvents, it was not the case for the PS core. Taking into account the volume occupied by each NPs in the different solvent, the concentration of NPs in suspension in DMSO needed to be increased in comparison to anisole. Even when comparing suspensions with a similar volume fraction of NPs, the suspensions in anisole behaved in a more solid-like manner and those suspensions were tougher, with significantly larger yield strain than the suspensions prepared in DMSO (Figure 7). The difference of yield strain cannot be ascribed to difference in the canopy architecture, even when taking into account the variation of the grafting density during the swelling of the PS core the samples prepared with the largest grafting density dispersed in anisole should be directly comparable to the particles prepared with the intermediate grafting density dispersed in DMSO the effective grafting density were 0.80 chains/nm$^2$ for PS$_m@$PMA in DMSO and 0.82 chains/nm$^2$ for PS$_h@$PMA in anisole. Since the PMA canopies had a similar structure in anisole and in DMSO, the conformation of the chain in the canopy was similar in both solvent thus interpenetration between adjacent particles should be the same in anisole and in DMSO. The main difference between the two systems was only the swelling of the PS core. The results suggest that having NPs with a soft core functionalized with a canopy of polymer favors the formation of tough and strong gels even at low concentrations.
Figure 7. Effect of the architecture of the PMA canopy on the properties of the colloidal gels formed with (i) \( C = 10 \) wt% or (ii) \( \phi_{cal} \) ca. 0.5 of \((\bullet)\) PS\(_h\)@PMA, \((\bigtriangleup)\) PS\(_m\)@PMA, \((\pi)\) PS\(_l\)@PMA and \((\theta)\) PS\(_h\)@PMA\(_{40k}\) in suspension in anisole (close symbol) or DMSO (open symbol).

Conclusions

In summary, a library of PS@PMA core-canopy particles with different canopy architectures, i.e., chain length \( (N) \) and grafting density \( (\sigma) \), was prepared at their behavior in suspension analyzed by rheology. The conformation of the end-tethered polymer chains transitioned from collapsed chains, to brushes, to stretched brushes and was influenced by the degree of polymerization, the grafting density and the solvent quality. Using selective solvent for uniquely for the canopy or a common solvent for the core and the canopy, suspensions with different behavior were obtained those with “hard core” and those with “soft core”.

Polymer-functionalized soft core NPs displayed similar trends as expected for more traditional hard core NPs. As expected, suspensions of soft PS NPs and soft PS@PMA NPs displayed a non-Newtonian behavior. The soft PS NPs formed jammed suspensions while for suspensions of soft PS@PMA NPs the interdigitation of the PMA canopy could be the main contributor to the shear thinning behavior. The viscosity of the suspension was governed by both the concentration of the NPs in suspension and the architecture of PMA canopy. The concentration at which the transition between the dilute and semi-dilute regime occurred shifted to lower concentration with increasing \( N \) and \( \sigma \).
As the concentration increased, the PS@PMA suspensions transitioned from a viscous liquid to a gel in which PS core as a junction point for the entangled grafted PMA chains. This transition was observed at lower concentrations for NPs dispersed in a solvent where both the core and the canopy were swollen. The key factor affecting the sol-gel transition of the PMA functionalized PS NPs was the number of MA units decorating the PS core, but the properties of the resulting gels were largely influenced by the architecture of the PMA canopy and the swelling of the core. More effective interdigitation between the particles occurred at high N and moderate σ due to the increased opportunity for canopy interpenetration. Gels were formed with either naked PS NPs or PS@PMA NPs with long PMA chains, where the interdigitation of the PMA canopy could be accomplished by chain entanglements, but not with PS@PMA NPs with short polymer brushes (N<200 methyl acrylate units) or binary mixtures of PS NPs and free PMA chains. It was found that the mechanical properties of the suspension, both moduli and yield strain, were affected by both the corona architecture and concentration of NPs in suspension. The direct comparison of soft-PS@soft-PMA NPs and hard-PS@soft-PMA NPs suspensions revealed that the soft NPs formed gels at lower concentration and that the gels at similar NPs content were stronger and tougher when the core suspensions prepared with hard core. These results provide information to tailor the behavior of polymer latex by controlling the architecture of a layer of grafted polymer to tune the rheological and mechanical properties of the latex suspensions.

**Conflicts of interest**

There are no conflicts to declare.

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