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Feature Article

End-functionalized polymers: Versatile building blocks for soft materials

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Abstract

We present a concise review of telechelic polymers of various architectures, focusing on the structure, solute solvent interactions, aggregation processes, equilibrium and dynamical properties and applications. Telechelics are macromolecules with functionalized, mutually attractive end-groups, which assume a variety of conformations that depend on solvent quality, salinity and pH of the solvent, as well as on the particular macromolecular architecture. In concentrated solutions, telechelic polymers offer unique possibilities to create novel materials with distinct rheological properties. Depending on chemistry and architecture, they can create percolating clusters and transient gels or they can show macroscopic phase separation into a dilute and a structured dense phase. The possibility to externally steer the morphology of these structures and the concomitant physical properties of the materials renders telechelic polymers into important and versatile building blocks for modern materials science.

Keywords: Telechelic polymers; Association; Computer simulations

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1. Introduction

Nowadays, polymers can be synthesized with specific properties that suit a diverse set of applications, ranging from medical devices to familiar consumer products. Macromolecular engineering offers the possibility to precisely control the molecular weight, the polydispersity and the design of specific polymer blocks, which selectively react with the solvent [1,2]. For instance, in the last decades there have been rapid developments of new radical polymerization techniques [3,4], which concern ionic, living radical and metathesis polymerization routes. In the present paper, we focus on end-functionalized or telechelic macromolecules. The term 'telechelic' originates from the junction of two Greek words: *tele* ($\tau\eta\lambda\epsilon'$), initially introduced by Josef Arens [5], in the 1968, means 'remote' while *chele* ($\chi\epsilon\iota'\lambda o\varsigma$) means lip, claw, nipper. Telechelics are defined as polymeric molecules with reactive terminal groups that have the capacity to form intra-molecular as well as inter-molecular bonds. While in most cases the term telechelic polymer is used when both ends of a polymer are functionalized, synthesized macromolecules here are considered as telechelics also when only a part of the chains is functionalized, e.g., a zwitterionic, low-functionality star, being able to associate intra-molecularly as well as to form bridges with other molecules. The simplest example of telechelics are triblock copolymers, ABA or more generally ABC, dispersed in the appropriate solvent, which promotes the aggregation of the terminal blocks [6]. In literature and in nature telechelic macromolecules with more complex architectures and geometries (spherical, cylindrical, lamellar) are present, due to irreversible synthesis (telechelic molecules)

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or reversible self-assembling (telechelic micelles) of polymeric end-capped chains in solution. In the last case, the number of triblock copolymers which form the micelle changes with the concentration becoming stable above a typical value dependent on the solution properties.

Although pioneering works seem to date back to 1947 [7,8], the concept of telechelic polymers was introduced in 1960 [9]. Significant contributions to the analysis of these systems increased in the last twenty years. There are several reasons for this great interest. From the experimental point of view telechelic polymers are useful for the synthesis of different size and block-sequences of multi-copolymers; telechelic groups can be used as precursor of chain extender and graft polymers. Moreover, they represent a fundamental model to understand intra- and inter-molecular aggregation processes and the relation between conformation and properties of different macromolecular solutions and materials. Indeed, due to the presence of different molecular interactions, such as hydrophobic and hydrophilic effects, van der Waals forces, Coulombic forces etc, self-organizing materials can give origin to vastly different structures and conformations with a large variety of properties relative to smaller surfactant molecules. This class of self-organizing materials, is of high importance and very promising for many practical purposes. For instance, a thorough understanding of biological materials, such as proteins and enzymes [10,11], has to take into account the creation of specific macromolecular conformations and structures and the possibility of self-assembly in several processes. The development of new devices in advanced technology industries, e.g., thermoplastic elastometers, pressure-sensitive adhesives, colloidal dispersants, compatibilizers of polymer blends, and foams, origins from the self-assembly of micelle-like aggregates, supramolecular structures, and solubilization properties of block-copolymers [12]. As we will discuss more in detail in the text, the research development on telechelic macromolecules is also of fundamental importance in several medical applications [13–19].

A classification of telechelics can be organized considering several factors: the geometry, the coupling between the different end-units and the solvent, the sequence and length of the reactive groups and in case of telechelic molecules the fraction of polymeric chains end-functionalized. In Section 2 we briefly present some details on the chemical/physical properties of the functional groups which capped the polymeric chains, briefly describing their coupling with the solvent and the model interactions, which account for their specific behaviour in solution. We emphasize that here, functionalized pertains to units which, on the basis of their specific, attractive interactions (polar, hydrophobic, H-bonding, dispersion etc.) can join and form intra- and inter-molecular connections in concentrated solutions, resulting thereby in responsive molecules and materials with tunable properties. In Section 3, our target are spherical telechelics, self-assembled telechelic micelles and telechelic dendrimers. Finally in Section 4 we focus on star-like telechelic micelles, which consist of telechelic polymeric chains chemically and irreversibly connected to the center by one end. Here the terminal groups in each chain are a small fraction of the total length. Finally, in Section 5 we summarize and draw our conclusions. We would like to stress here that the domain of telechelics is huge. As an obvious consequence, in this work we underline only some experimental and theoretical results and tools connected to practical and specific applications.

2. Functional groups: synthesis and properties

There are different techniques to prepare telechelic polymers with terminal groups via a variety of reaction mechanisms of different complexity due to functional groups present in reacting compounds and their inherent steric effects. Some examples are ionic polymerization, conventional radical polymerization, polycondensation and controlled radical polymerization (CRP) [20–25,27]. Among these methods, ionic polymerization is usually characterized by narrow dispersity and suited to produce very regular polymers [26]. CRP becomes a new technique that may generate polymers of controlled molecular weight and it may be carried out in the presence of many functional groups from monomers, initiators, or chain transfer agents [22,25,28–33]. In particular, reversible addition-fragmentation chain transfer-mediated radical polymerization, a typical type of CRP, has been used to prepare well-defined polymers with predetermined molecular weight and narrow polydispersity [30–33]. Finally, several direct methods can be combined in such a way to obtain telechelics with extremely low polydispersity and defined chain lengths. As far as the physical origin of the attraction between the end-groups is concerned, again, varieties of possibilities are offered. The most common case is one in which the end-groups are hydrophobic whereas the backbones of the rest of the chains are hydrophilic. This is particularly relevant for telechelic polyelectrolytes, whose backbone is water-soluble and whose charge and overall conformation can be tuned by modifying the pH and the salinity of the solution. This leads to a variety of conformations and the appearance of sol–gel transitions and transient physical gels in concentrated solution, as discussed in the recent work of Bossard et al. [34]. The specific polymer employed there was a long PDMAEMA polyelectrolyte capped by short PMMA blocks [6]. Apart from hydrophobicity, a number of distinct interactions, such as hydrogen bonding, thermodynamic and van der Waals forces [35–40] can also dictate the behaviour of end-groups. A particularly intriguing possibility is to employ at terminal monomers dipolar, zwitterionic groups [41,42]. These lead to a variety of intra-molecular conformations and the emergence of transient, physical gels with tunable properties in concentrated solutions. When grafted on planar, hard surfaces, the resulting telechelic brushes attract each other when they come into contact [43], a feature that has been theoretically explained via a mechanism of entropic gain through the recombination of telechelic chains belonging to different surfaces [44].

3. Telechelic macromolecules

Telechelic, branched macromolecules, such as star- or dendrimeric-shaped (see, e.g., Fig. 1), reveal extremely peculiar

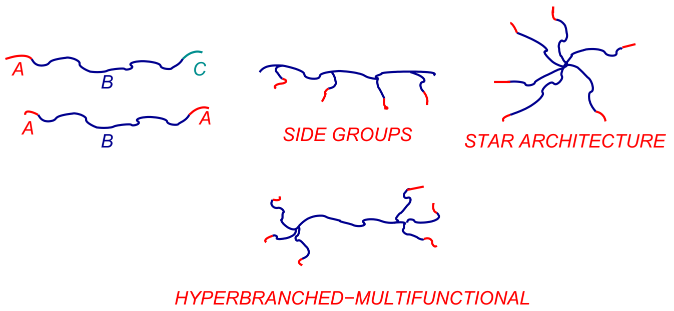

Fig. 1. A schematic representation of telechelics: on the top, from the left we display diblock and triblock copolymers, a polymer chain with telechelic side groups and a telechelic star-like polymer. On the bottom we show a telechelic dendritic polymer. Redrawn from http://www.chem.cmu.edu/groups/maty/.

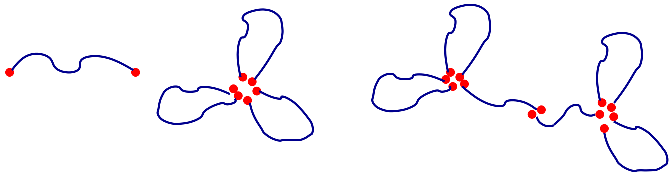

Fig. 2. From the left to the right: schematic representation of the self-association of telechelic chains in a flower-like micelle above a critical concentration value (middle), and of a typical inter-molecular aggregation between micelles at high concentration (right). Redrawn from Ref. [53].

topology and properties and represent useful models to study intra- and inter-association processes in nature. As anticipated above, functionalized systems (assembled micelles as well as synthesized molecules) are particularly important in the context of drug delivery, host–guest chemistry, chemical catalysis, clinical therapies and more in general medical applications [13–19]. Fundamental aspects of such macromolecules are their size and structure, which are comparable with those of biological systems. Moreover, the addition of selectively reactive groups to polymeric systems results in a larger sensitivity to environmental factors, such as pH, solvent quality, and temperature, which allows for a better control of their conformation [17,45]. In this work, we focus on three classes of telechelics: spherical self-assembling telechelic polymers, telechelic macromolecules with dendritic shape and telechelic star polymers. In this section we analyze the first two classes, i.e., spherical telechelic micelles and dendrimers, giving some examples of experimental and theoretical studies which mainly concern some practical aspects and applications. In the next section, we consider in detail telechelic star polymers.

3.1. Spherical self-assembled telechelic chains

The study of the principles behind the aggregation of self-associating polymers (see, e.g., Fig. 1), carrying one or more strongly associating terminal groups, has attracted strong interest in recent years [46–48]. In particular, considerable progress has been achieved in synthesizing telechelic polymers with a designed number and positions of the specific reactive groups [1,20–25,27]. Some examples are amphiphilic polymers or solutions of ionomers in organic solvents. In these systems, the aggregation is forced by an effective immiscibility of the components of the polymer chain. The inter- and intra-molecular chain-linking process with appropriate telechelics can create a variety of complex architectures and supramolecular structures, with desired dynamical and rheological characteristics. In particular, when the associative ends of telechelics are much shorter than the backbone, spherical micelles always form (see Fig. 2, middle). As anticipated in the previous section, the specific structure and properties of the aggregates depend on the solvent–solute interaction and on their relative volume fractions. The obstructions to the aggregation process arise from the low concentration of a small number of terminal reacting groups along the chain, the excluded-volume effects and the steric hindrance present in the interaction between polymers [2]. The overall low concentration problems can be circumvented by introducing electrostatic interactions in polymer chain blocks. For instance, in Ref. [1] the authors considered electrostatically self-assembled polymers with two pyrrolydinium salt groups (cationic chains) or two carboxylate groups (anionic chains), at the ends or at designed interior positions, and subsequent covalent fixation. Depending on the position of the reactive groups and the combination of the cationic and anionic chains, several different topologies could be produced: ring polymers, as well as one-tail and two-tail tadpole macromolecules. In Ref. [49], the effect of zwitterionic substitution on diblock and triblock copolymers has been studied with rheological and dielectric spectroscopy and SAXS experiments to explore the aggregation of the terminal groups and the dynamics. The aggregation processes strongly influence the electron density profile. The last example of telechelics we mention, without of course exhausting the entire class, regards associative polyelectrolytes in aqueous solutions. In particular, photon correlation spectroscopy in solution of hydrophobically associative polyelectrolytes [polystyrene-*block*-poly(sodium methacrylate)-*block*-polystyrene], has been performed and reveals the formation of supramolecular structures consisting of finite-sized microgel particles [50]. The size of the cluster increases with the concentration, approaching the macrophase separation region, where a transient physical gel coexists with the solution of supramolecular clusters. We stress here that, in general, water-soluble associative polymers are interesting for several practical ecologically friendly technologies used in medicine, food and cosmetic industries, coatings, etc. More particularly, polyelectrolytes comprise several natural polymers occurring in living systems.

Theoretical and simulation work in this direction has considered long water-soluble chains with insoluble small groups in appropriate solvent or, more generally, homopolymers carrying a certain fraction of thermally reversible stickers [51–59]. In Refs. [55–57], emphasis was put on the macroscopic phase behaviour of concentrated solutions of associating polymers that either carry stickers along their backbones [55,56] or they are amphiphilic and can carry the attractive groups either at the ends or at the middle of the chain. An intricate interplay between micellization vs. macroscopic phase separation, as well as the occurrence of sol–gel transitions was found, whose competition sensitively depends both on the number and the location of the attractive groups or stickers. In general, it can be stated that depending on the attractive/associating blocks' number, their nature, and their size, either a single molecular micelle or a string of such micelles can form. Let us focus on telechelic chains: by means of scaling arguments and on the results obtained for star polymers [60,61], the authors of Ref. [52,53] studied the conformation of the single macromolecule. In Ref. [62], the problem of a quantitative determination of the radius and aggregation number of the micelles has been discussed. In particular, the authors calculated the contributions to the free energy from the interface, stretching of the chains, and excluded-volume interactions [63,64], and minimized the resulting expression to determine the most probable aggregation number. In this study, the polydispersity has also been considered and accounted for most of the discrepancies with experiments. Also, the equilibrium and dynamical properties of telechelic micelle solutions in the limit of high aggregation number has been analyzed (see, e.g., Ref. [53,65]). Above a certain critical micelle concentration (cmc), the amphiphilics associate in flower-like micelles (see Fig. 2, middle), which strongly attract each other in a diluted regime. The important new feature here is the possibility to form bridges between terminal groups of different molecules (Fig. 2, right side), which gives rise to a strong attraction between micelles [66,67]. At high concentration, these then form a reversible gel, in which the (partial) flowers are connected by multiple bridges. In this regime, the dynamics is driven by the bridge-loop exchange rate and by the effective barrier associated to the deformation/compression of the molecule. The viscosity shows a sensitive dependence on polymer concentration ϕ around $\phi \cong \phi^*$, the value corresponding to the overlap polymer concentration inside the micelle. Above ϕ^* the viscosity increases exponentially and then it can decrease in a limited concentration range [53]. The qualitative results are valid not only for telechelic chains but also for polysoaps and multiionomers, containing many insoluble groups per chain.

We conclude this section by briefly mentioning two situations, which differ in some aspects from the other systems discussed here but are nevertheless very interesting from the point of view of biological and technological applications [68], e.g., to solubilize enzymes, catalyze biochemical reactions, in nanocluster synthesis etc. We consider first a more complicated situation, pertaining to a *ternary* soft mixture: a polar medium (such as water), a nonpolar organic solvent plus amphiphilic polymers. The main role of the polymers in such a condition is to reduce the interfacial tension between polar and nonpolar solvent, favoring an increase of the corresponding interface area. The aggregation of chains with a single sticker can stabilize microemulsions of micelles. If the good solvent for polymers is in excess, then it is possible to have the so-called reversed micelle, i.e., a three-layer aggregate, which consists of low-molecular-weight solvent droplets, surrounded by a compact polymeric corona (stickers plus polymers) and immersed in the external solvent medium. The compact corona originates from the attraction of the end-groups. The potential of this system for medical applications (e.g., drug delivery) is clearly strong and justifies the large numbers of studies in this area. For instance, the structure of such aggregates has been studied via Monte Carlo simulations using the bound fluctuation model [69]. The authors analyzed the typical three-layer structure described above and the stability and the thermodynamics of the micelle formation in the presence of low-molecular-weight solvent particles, which interact attractively with the end monomers. Micelles are supposed not to interact with each other (in the low concentration limit). As solvent particles are included inside the micelles, the core disintegration temperature increases with respect to the simple aggregate of amphiphilic chains. A higher concentration of solvent particles inside the core increases the association number of chains in the aggregate. The reverse micelle properties, such as penetration of external solvent into the corona, average shape and associated fluctuations etc. are very important in practical applications, including catalysis or separation of microscopic particles and rare earth elements [69].

Further, we underline the relevance of the study on the interaction between nanometric colloidal particles and molecular chains with selectively adsorbing groups. Theoretical modeling of this phenomenon is important to understand polymer stabilization and flocculation processes, important for waste water treatment, nanoparticle toxicity and other environmentally relevant applications. In Ref. [70], the authors analyzed polymers with several reactive groups, which adsorb on nanoparticles and can strongly attract each other, by using Monte Carlo simulations and simulated annealing. In the case of telechelic chains (only two reactive end-groups per chain), it was found that the small adsorbing particles play the role of bridge points, which bind together the functional groups of two different polymers. Below the critical temperature there are mixed clusters containing colloidal particles and stickers. This direct or indirect binding determines a web-like structure. In addition, the transition temperature of structure formation is increased compared to systems without mutual end-groups attraction. At sufficiently strong attraction between colloids and end-groups, most of the telechelics adopt a loop-like and/or stretched bridge-like conformation. The resulting structure is a reversible network of flowers, connected by one or several bridges. Decreasing the temperature increases the size of the mixed clusters in which the particles and the functional groups pack locally on a binary grid corresponding to crystal-like arrangement.

3.2. Telechelic dendrimers

Dendrimers are monodisperse, tree-like hyper-branched polymers with a central core, internal branching layers, and a large number of terminal groups; their overall number of monomers grows exponentially with total generation number g, a feature that practically sets an upper limit $g = 10$. Important dendrimer properties are low polydispersity, high solubility, as well as low viscosity of dendrimer solutions; similarly to other branched or star-shaped polymers [71–77], dendrimers show glass transition parameters that differ from those of their linear-chain counterparts. To give an impression of the real structure of a dendrimer (as opposed to the two-dimensional, chemical representation of the same), we show in Fig. 3 a typical simulation snapshot of a fourth generation dendrimer. By functionalisation of the end-groups of dendrimers, the structure and the behaviour of these particles in solution can be altered and tuned according to specific needs.

Recently, dendritic polymers composed of the natural metabolites glycerol and succinic acid were synthesized, functionalized (e.g., with multiple copies of drug molecules such as methotrexate), and evaluated as new medical materials [16]. Dendritic unimolecular micelles with a hydrophobic core surrounded by a hydrophilic shell are used in drug delivery systems [16,78] providing an internal space to encapsulate medical agents. The core of such dendrimers contain *pockets* that are capable of localizing hydrophobic molecules, as opposed to flexible, self-avoiding dendrimers in good solvents, which show no holes in their interior and assume rather a dense-core configuration due to backfolding of their terminal units in the interior of the molecule [71,79,80].

Some dendrimer properties play a key role in elucidating their relevance as drug delivery vectors [81]. Unlike amphiphilic block-copolymers micelles, dendrimers do not have problems of stability below a typical critical micelle concentration. In diluted solutions, such as in the human body, amphiphilic copolymers can dissociate in free chains releasing prematurely entrapped drugs. On the contrary, amphiphilic co-dendrimers can form so-called unimolecular micelles, where the copolymers are covalently attached to each other. In other words, when dendrimers possess terminal groups that are either charged or polar, they can be considered as static, covalent micelles. For this reason, the micellar character of the structure is maintained at all concentrations. Moreover, dendrimers can have a high number of terminal groups to be functionalized.

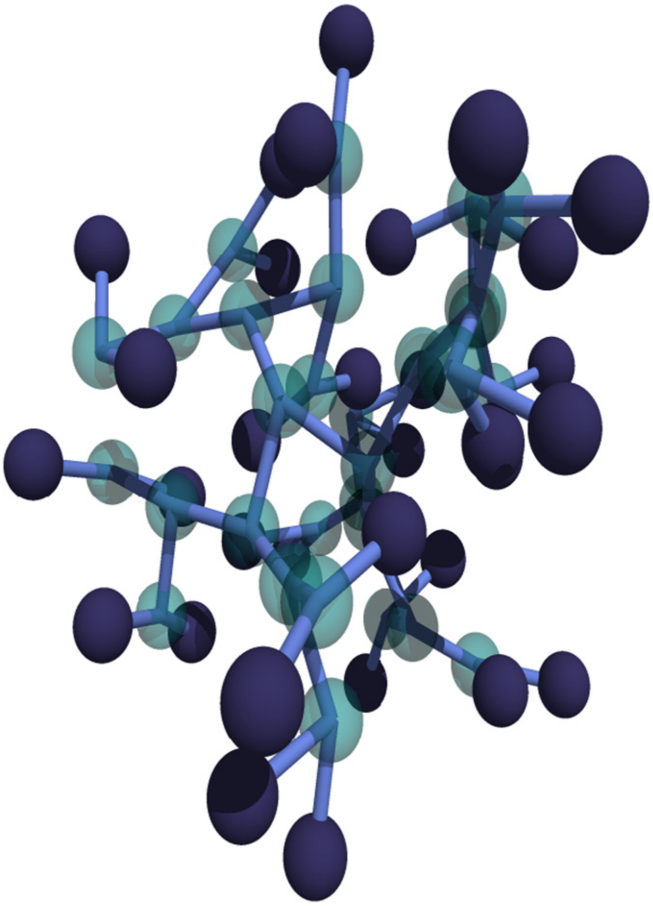

Fig. 3. Simulation snapshot of a dendrimer of fourth generation. The dark spheres are the terminal reactive groups while all the other monomers appear as semitransparent spheres. The bonds between the monomers are rendered as cylinders.

Standard off-lattice and biased on-lattice Monte Carlo simulations have been performed to study the conformation of amphiphilic dendrimers for which terminal monomers and internal monomers interact selectively with the solvent (being chemically different) [45,81]. In Ref. [81], the authors analyzed amphiphilic diblock dendrimers with single and binary trifunctional core, generation numbers $g = 1, 4, 5, 7$ and different number of spacers between branch points. The interaction model includes connectivity between bounded monomers via harmonic springs, Lennard–Jones (LJ) potentials between every couple of monomers and hard-sphere short-range repulsion to exclude efficiently the particles' overlap. Two kinds of dendrimers were considered in Ref. [81], those with internal hydrophobic (H) block and external polar (P) monomers, termed Inner-H, and those with an inverse architecture, termed Outer-H. The strength of the LJ potential changes according to the specific H–H, P–P, H–P interactions, modeling implicitly the solvent. In both the cases studied, Inner- and Outer-H, the authors found unimolecular and loopy micelles for low generation value, and cigar shapes for high generations ($g > 4$), which are more elongated in the Outer-H topology, see Fig. 4.

For a binary core, *dumbbell*-like conformations appear. This phenomenon involves dendron segregation at the core of the large co-dendrimers. On the top of Fig. 4, we show a 2D schematic representation of a $g = 4$, binary core, Inner-H, co-dendrimer. The polar monomers are smaller for visual clarity. On the bottom we can observe a typical simulation snapshot for a cigar-like conformation of a $g = 7$ binary core, Inner-H co-dendrimer. In both parts of the figure, the different colors distinguish monomers belonging to separate dendrons.

In Ref. [45], the authors complement and go beyond the previous model. Focusing on $g = 3$ and $g = 6$ generation dendrimers, they model short-range repulsion by imposing a self-avoiding walk condition and the attraction via the nearest neighbor contact energies between particles. The conformational phase diagram depends strongly on g and on the contact energy between internal/terminal monomers and the solvent. In addition to the scenario investigated in the above mentioned work, they allow the interaction parameters between internal/terminal monomers and the solvent to assume negative values, which mimic attractive polar interactions, such as hydrogen bonding, between particles. In this last case, they observe more exotic dendrimer conformations, e.g., spontaneous development of asymmetry where the core monomer is left exposed at the periphery of the molecule, and strong dendron segregation. From their study, the authors of Ref. [45] suggest

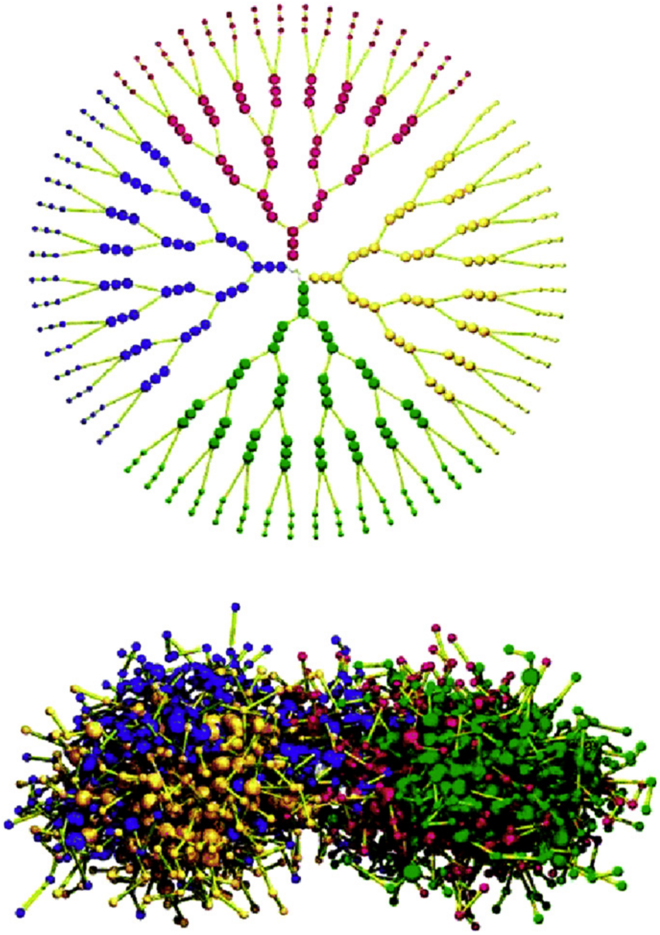

Fig. 4. Top: 2D schematic representation of a $g = 4$, binary core, Inner-H, co-dendrimer. The polar monomers are smaller for visual clarity. Bottom: typical simulation snapshot of a cigar-like conformation of a $g = 7$ binary core, Inner-H, co-dendrimer. In both the figures the different colors distinguish the monomers from separate dendrons (reproduced from Ref. [81] by permission of the authors).

a way to control the access to the molecule core, e.g., by exploiting the transition between the spherical symmetric state and the asymmetric micelle state or the transition between the separated and nonseparated dendron states [45].

4. Telechelic star polymers

Telechelic star polymers are molecules made of polymeric chains with one end chemically linked to the star center while the other end is functionalized. Block-copolymer stars with a hydrophilic core and a hydrophobic corona [82,83] can also be included in this class when the length of the hydrophobic part is a small fraction of the whole chain.

Recently, progress in the synthesis of telechelic star polymers have been achieved in various directions. Star-shaped tri-, tetra-, penta-, and hexa-arm poly(L-lactide)s with pyrene (lipophilic) terminal groups have been synthesized and studied. The spectral analysis of the static and dynamic segmental motions in polar solvent, at room temperature, evidenced end-to-end ring structure accompanied by intra-molecular excited dimer formation [84]. The probability for excimer formation increases with the functionality and decreases with the number of monomers per arm. The localization of the pyrene-associated groups with respect to the star center changes with the arm number. Similar systems were also analyzed in terms of structure and thermal properties with X-ray diffraction and differential scanning calorimetry [85]. The interest in such systems originates from the hydrolytical and biological degradability, biocompatibility and good mechanical properties of the lactides. They are employed as slow-release drug delivery systems, bioresorbable surgical sutures, in surgical implants etc. Other examples of synthesized telechelic star polymers are poly(ethylene-*co*-propylene) polymers bearing terminal self-complementary multiple hydrogen-bonding sites [86], which exhibit higher viscosity and high associated structures relative to non-functionalized analogues, and asymmetric three-arm stars comprised of polyacetylene and polystyrene blocks [87]. Moreover, macromolecules with polar end-groups have been synthesized and provide a simple system to study the mechanism driving intra- and inter-aggregation properties [41,42,88–97]. In particular, three-arm polybutadienes stars with one, two or three chains end-functionalized with zwitterionic groups have been prepared by anionic polymerization [96]. The different samples are schematically represented on the left of Fig. 5, including the possible inter- and intra-molecular association processes (right).

Low-angle laser light scattering and membrane osmometry techniques have been employed to analyze the dilute regime [96]. Scattering experiments have shown that at fixed number of monomers per arm the degree of inter-association in solution increases with decreasing the number of zwitterionic groups (per molecule). Indeed, at low concentrations the multifunctional stars tend to interact intra-molecularly rather than inter-molecularly. For fixed functional groups the inter-association decreases by increasing the arm molecular weight [96] because of the excluded-volume repulsions of polymers. The

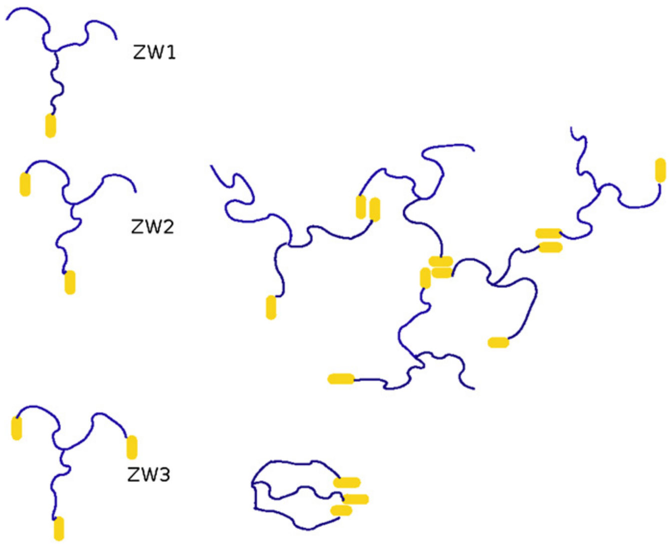

Fig. 5. Left: molecular structure of the zwitterionic end-functionalized three-arm star polymers. Right: self-organized supramolecular structures of the di- and tri-functionalized polybutadiene stars. Redrawn from Ref. [41].

aggregates are in general polydisperse. The samples show a less strong association relative to linear zwitterionic chains, due to the steric interactions originated from the star structure (one functional group) and the intra-molecular association phenomenon (two and three functional groups). In more concentrated solutions, there is gel formation.

Successive dynamic light scattering experiments and viscometry measures confirmed the above-described scenario and have been applied to more concentrated domains [97,41]. X-ray scattering and rheological experiments support the same trends with respect to the number of functional groups and polymerization, all the way into the melt. To resume: in diluted samples the stars self-assemble into distinct supramolecular structures, which for trifunctional stars include collapsed, soft-sphere conformations. At high concentration the formation of transient gels has been observed for multifunctional samples with the characteristic of the network depending on the molecular weight of the arms [41].

The functionalisation of star polymers by strong polar terminal groups bears the opportunity to obtain many different supramolecular structures and respective dynamic responses by controlling well-defined parameters such as the number of functional groups, the length of the chain and the arm number of the stars. The experimental efforts on these systems open clearly the route for design and development of new biological materials with complex architectures.

The mechanisms driving conformational and structural changes in these macromolecules have also been analyzed from the theoretical point of view. The analysis includes monomer-resolved molecular dynamics (MD) simulations and scaling-based theory [98,99]. In the simulation model, the authors considered different contributions to the particle–particle interactions: connectivity FENE-like potential between nearest neighbor monomers in the same chain, purely repulsive Lennard–Jones interactions between every monomer and full Lennard–Jones interaction between functionalized monomers [98]. The attraction between terminal monomers is long-ranged and gives a good representation of the polar molecules studied in Refs. [96,97,41,42]. The main parameters controlled in Refs. [98,99] are the length and the number of the chains per molecule and the temperature; the solvent is implicitly considered and all the chains are functionalized. The ranges of parameters studied are $1 \lesssim f \lesssim 10$, $19 \lesssim N \lesssim 200$, and $0 < T^* < 1.3$, where f and N stand for the functionality and number of monomers per arm, respectively, T^* represents a reduced temperature. In particular, in Refs. [98,99], the conformational properties of the single macromolecule have been analyzed by studying the radius of gyration, the attractive energy evolution during the simulation runs, the radial distribution function and the free energy pertinent to various candidate conformations. The model can be easily adapted to describe different selective reactions of the terminal monomers with respect to the full-body monomers, by changing, e.g., the range and the shape of the attractive and repulsive terms, as for ionic telechelics, for which the attraction strength can be tuned by changing the salt concentration and/or the solvent dielectric constant.

In Fig. 6, we show a typical snapshot of high temperature telechelic star polymer obtained via molecular dynamics (MD) simulation. For high temperatures the star configuration is exactly the same as that for normal stars, i.e., in the absence of attractive groups [99]. This is reasonable, since in this case the attractive binding energy is ‘‘washed out’’ by the thermal one or, in different terms, entropy dominates over energy in the free energy considerations of the system. Decreasing the temperature, the end monomers start to strongly attract each other. In Fig. 7, we exemplarily display the full range of possible conformations for $f = 4$ and $N = 10$ [98], from the left we can observe the open star configuration, a two-tail tadpole, the two-ring configuration (with two accumulation points of end monomers), a partially collapsed structure plus a free chain (three end monomers associated) and finally the collapsed water melon structure. The temperature below which the system collapses and all the terminal monomers form a single aggregate decreases with the number of monomers per chain and increases with the arm number, see Fig. 8.

The trends are valid in the whole $f \leq 10$ range. However, in the collapsed configurations for $f < 7$, the chain ends tend to associate by forming *regular polyhedra*, trying to minimize the distances between every pair of monomers, whereas for

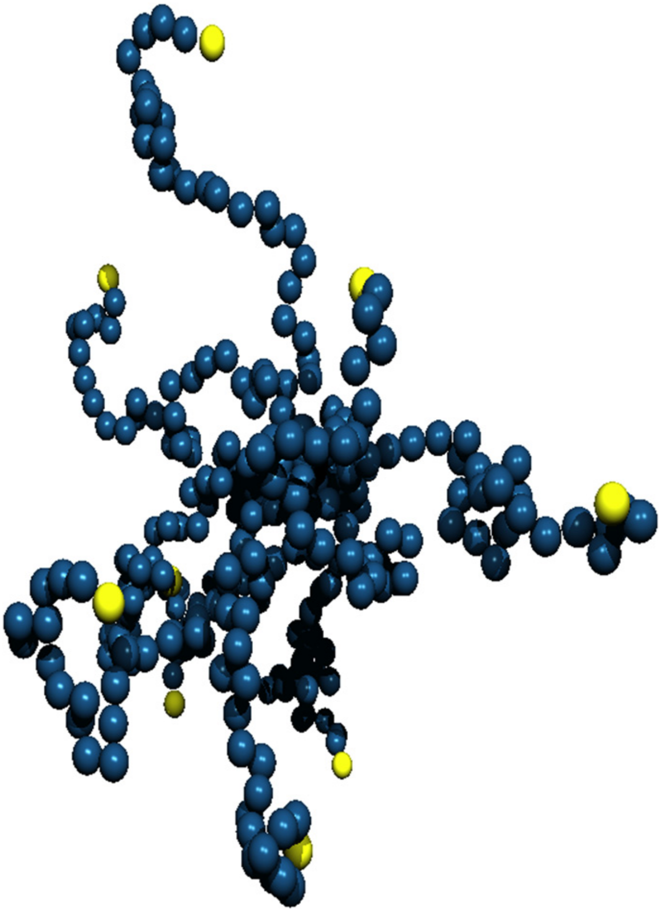

Fig. 6. Open star configuration for a telechelic star with $f = 10$ arms and $N = 30$ monomers per arm at reduced temperature $T^* \equiv k_B T/\epsilon = 1.2$, where k_B is Boltzmann's constant and ϵ the depth of the attractive well between end monomers.

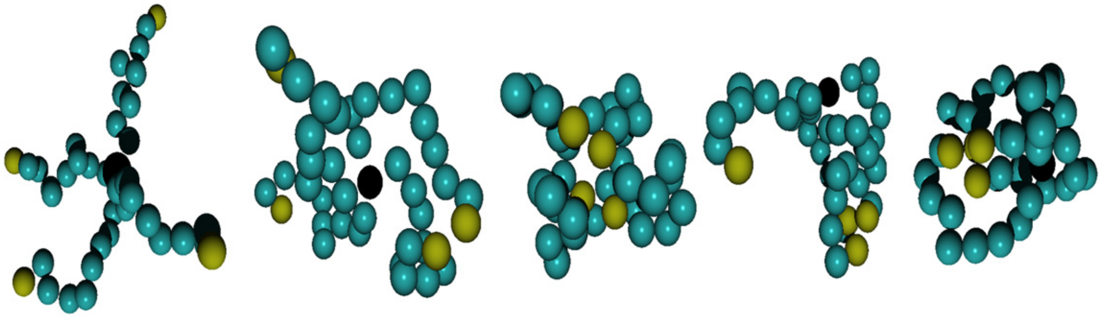

Fig. 7. A succession of possible conformations for $f = 4$ and $N = 10$. Notice the gradual collapse of the star from an open to a water melon conformation.

higher f they arrange in consecutive shells of neighbors, the last being appreciably far apart from the others. As a consequence, the aggregate is more fragile and instead different configurations with partial aggregates result [99]. In the systems considered here, as already discussed above, the aggregation properties depend on a complicate balance between entropic and energetic contributions to the free energy such as elastic energy, excluded-volume interactions and van der Walls attractions between terminal groups. To complement the MD study a scaling theory has been developed for low-functionality stars [98], on the basis of which the different possible conformations have been analyzed. This way, the parameter-dependence of the free energy contributions has been quantitatively analyzed. In particular, the theory gives evidence of only two stable configurations for $f < 6$: the open star configuration (high temperature) and the water melon configuration which the molecule exhibits below a certain temperature (see panel of Fig. 8). The trends described with the theoretical study and with the simulations are summarized in Fig. 8 for small arm number and agree with the results obtained in experiments on tri-zwitterionic macromolecules.

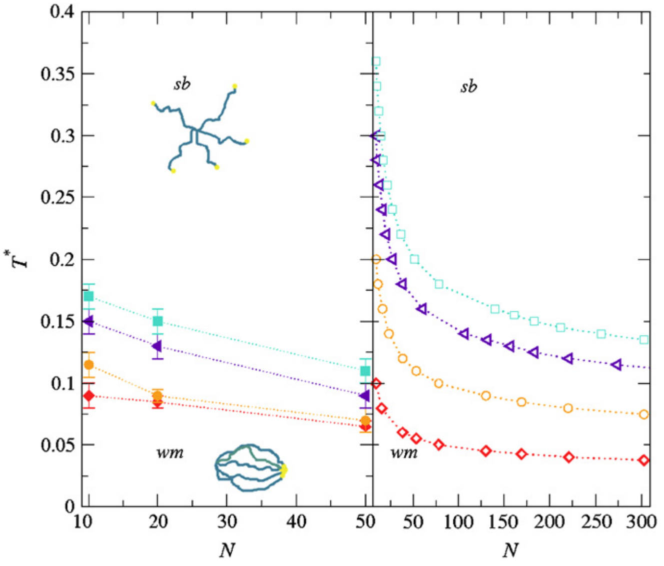

Fig. 8. Regions of stability of the star-burst and water melon configurations vs. the number of monomers per arm, from bottom to top, $f = 2$, 3, 4, and 5. Left panel: results obtained from MD simulations. Right panel: results obtained by employing the scaling theory developed in Ref. [98].

Related are also the extensive Monte Carlo simulations of Refs. [82,83], in which the authors consider block-copolymer stars with both telechelic (end-attractive) and the opposite (core-attractive) monomers, which have been, respectively, termed Outer-H and Inner-H. In the limit of a small fraction of hydrophobic (H, attractive) units in the Outer-H architecture, the copolymer stars studied in Refs. [82,83] indeed become very similar to telechelic stars. Both an end-collapsed conformation (termed ‘type B’, for small functionalities f) [82,83] and a conformation with many partial water melons for high f values (termed ‘type C’) [83] have also been seen there, corroborating thereby the stability of those through an independent approach. The possibility to form an empty-collapsed capsule can be analyzed in the contest of biomedical applications such as vehicles able to encapsulate drugs and/or to inhibit the adsorption of substances in the body (e.g., lipids). Also in this case, as for dendrimers, stability problems do not exist for low concentrations. The molecule can be in principle synthesized with functionality and number of monomers able to stabilize a capsule for the appropriate temperature. Finally, as in the previous cases we discussed, the great tunability of these molecules open the way to design new materials with specific dynamical characteristics. At low temperatures and near the overlap concentration various types of gels can appear, with viscosity properties due either to transient network formation or to the existence of entangled loops. Work along the lines of investigating telechelic star polymers solutions by means of computer simulations is currently in progress [100]: the ability to control the growth and size of finite, stable clusters/aggregates is really important, e.g., in flocculation problems related to the waste water treatment, nanoparticle toxicity etc.

5. Conclusions

Macromolecules with end-functionalized groups, akin to surfactants and to block-copolymers, can be synthesized in a variety of architectures, sequences between the various groups and length of the respective block units. At low concentrations, and crucially depending on the macromolecular architecture, these can assume a variety of conformations, ranging from the formation of flower-like micelles, to open dendrimers to water melon like, hollow objects. As the concentration grows, self-organization of hypermolecular units sets in, which can result in the development of liquid-like structure among the micelles, the formation of reversible, transient physical networks through the establishment of inter-molecular bridges [101] or to macroscopic phase separation. The ensuing physical properties can be tuned by suitable changes of parameters such as temperature, pH or the salinity of the solution and thus open up the way for the manipulation of materials and their rheological properties. The range of applications is vast and the full theoretical understanding behind the mechanisms driving a sensitive balance between competing interactions is still lacking for a large number of these novel and exciting materials. More work is needed, on the simulational and the theoretical front in order to achieve the goal of a bottom-up construction of materials using telechelic polymers, upon which the design of suitable building blocks will lead to soft solutions with desired macroscopic properties. The goal here is to tune the rheological response of the material by being able to control the formation and dissociation of bridging bonds and networks in the macroscopic sample, an ability that will allow for steering of viscosity and elastic response of the system.

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