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Feature Article

Selective crosslinking or addressing of individual domains within block copolymer nanostructures

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ABSTRACT

Block copolymer nanostructures are an intriguing class of materials and during recent years increasing interest is being devoted to develop strategies for site-selective chemistry within one of the constituting domains. One of the most frequently employed strategies is crosslinking, either permanently (through, *e.g.*, radical crosslinking), by introducing reversible covalent bonds, or *via* electrostatic interactions. In addition to crosslinking, the selective addressing of suitable building blocks by hydrogen bonding or the introduction of functional groups at junction points between adjacent segments broadens both the range of accessible morphologies as well as the toolbox for interface modification. We try to provide a brief overview why addressing individual domains is of interest and highlight recent progress for the most prominent approaches. Further, we selected two application fields, which (to our opinion) represent exciting areas of research and, at the same time, have benefitted tremendously from recent progress in (block co-) polymer chemistry. In both cases we expect significant progress, either in terms of substrate scope for block copolymer membranes or regarding the bottom-up design of interfaces in nanostructured hybrid materials.

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1. Introduction and scope

Over the last decades polymer chemistry has moved away from merely developing new or broadening the scope of existing polymerization techniques and methodologies [1,2]. Instead, increasing efforts have been devoted to realize previously inaccessible monomer combinations *via* method crossover, post-polymerization modifications [3–6], innovative protection-deprotection strategies, sequence control [2], or macromolecular conjugation reactions [7,8]. Polymer science has always been tremendously interdisciplinary and thus located at the interface of different scientific disciplines, including biology, biochemistry, medicine, physics, and materials science. This has become even more accentuated through recent developments.

Initially being regarded as rather exotic materials, more and more research groups develop interest in block copolymers, a material class where at least two different monomers are arranged in a sequential manner. By this, one single material can combine the properties of all involved monomeric building blocks and, in addition to statistic, random, or gradient copolymers, the intrinsic immiscibility of unlike polymeric segments leads to microphase separation and a very facile access to nanostructured materials in different environments, *i.e.* in the bulk or in solution [9,10]. Thereby, both domain size and morphology can be precisely adjusted by molecular parameters of the involved building blocks such as molar mass, volume fraction, architecture, and segment rigidity. Whereas this has been known for quite some time, in recent years increasing efforts have been undertaken to not only create nanostructured materials, but to either control the assembly process itself [11] (and thereby most often the outcome) or to exploit suitable chemical tools to address individual domains within such materials. Finally, if a common term is to be found for all of these approaches, in our opinion this can be well unified as *creating, manipulating, and addressing interfaces*. In that respect, the term *interface* relates either to polymer-polymer, polymer-surrounding medium, or polymer-metal interfaces and, intricately programmed by their segmental heterogeneity, block copolymers represent ideal candidates to perform reactions at or modifications of interfaces. Pushing boundaries, in the extreme case this can result in addressing certain areas along a single polymer chain, for example in approaches to force polymer chains into defined geometries *via* stepwise folding under high dilution. This requires either the precise positioning of functional groups or orthogonal binding motifs at specific monomer sites or [12,13], *e.g.* at the junction of two segments in block copolymers [14–16] or, which has become a quite vibrant area of polymer chemistry, control over monomer sequence in copolymers or polypeptoids [17–20].

Probably the most well-studied and at the same time simplest approach to address individual domains is to exploit site-selective chemistry for the crosslinking of one specific segment in nanostructured materials. With regard to block copolymers, this has been frequently used to "lock" bulk morphologies (which might not always be in thermodynamic equilibrium) [21,22], to transfer such structures to the solution state [23], or to prevent disassembly of block copolymer micelles upon dilution below the critical micellization concentration (cmc) [24,25] or transfer into a non-selective solvent [26].

In thin films, earlier examples mainly focused on stabilizing block copolymer nanostructures to create more robust and, concomitantly, more effective templates [1,27]. This has been used for the formation of mesostructured silica and titania [28], the preparation of monolithic structures [29], or for studying the effects on mechanical properties, conformational freedom of specific segments [30], or bulk morphology [31]. With regard to the self-assembly of block copolymers in selective solvents, one of the first examples of crosslinking was demonstrated by Procházka and coworkers [32]. They added dibenzoyl peroxide as photoinitiator to micellar solutions of polystyrene-*block*-polybutadiene-*block*-polystyrene (PS-*b*-PB-*b*-PS) triblock terpolymers in mixtures of THF and 2-methoxyethanol. Micelles with a PB core were formed and, after crosslinking using UV irradiation, the aggregates could be preserved in THF as non-selective solvent. Afterwards, many examples appeared where either core [33], shell [34], or corona of micellar nanostructures with different morphology had been crosslinked using different techniques [35,36]. Thereby, the majority of examples addressed the micellar core to control stability and/or applicability of these nanomaterials in different environments. Fewer efforts have been devoted to shell or corona, such as Hales et al., who achieved crosslinking at the core-corona interface using α,α'-azoisobutyronitrile (AIBN) [34] or Rupar et al., who crosslinked the polyisoprene (PI) corona of segmented core-crystalline rod-like micelles as an intermediate step to enable the formation of asymmetric block comicelles (this will also be discussed in more detail later) [37]. Also, crosslinking of micellar compartments can drastically affect efficacy of such nanocarriers for drug delivery applications [38] or in photodynamic therapy [39].

Another distinction has to be made in whether introduced crosslinks are permanent or not. Whereas irreversible crosslinking can be favorable if mechanical stabilization or an increase in robustness towards different solvents is required, other application fields might benefit from dynamic and, thus, reversible crosslinks [40,41]. One example clearly are materials with (self-) healing characteristics, *e.g.* consisting of dynamic covalent networks or ionic clusters [42–45]. Here, the formation and break-up of crosslinks and with that material dynamics can be controlled by intrinsic material properties such as glass transition temperature or external stimuli like pH [46], temperature [47], or irradiation with light of a suitable wavelength [48,49]. Such approaches are also suitable for the selective crosslinking of distinct areas in block copolymer nanostructures, however, examples demonstrating this to date are rare and include reversible complexation of boronic acid functionalities [50] or site-selective Diels-Alder chemistry in block copolymers [51].

With this perspective article, we try to both show the reader the current scope of domain-selective chemistry in block copolymer-based materials as well as pinpoint current limitations and prospective future directions. We specifically concentrate on materials formed from block copolymers and how one individual domain can be selectively crosslinked, either in a reversible or irreversible manner. Thereby, particular focus is put on how this can be exploited to tune materials properties, adjust (nanomaterial) stability in certain environments, or create structures that can serve as robust and versatile templates.

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