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Review

Design and Application of Nanoscale Actuators Using Block-Copolymers

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Abstract: Block copolymers are versatile designer macromolecules where a "*bottom-up*" approach can be used to create tailored materials with unique properties. These simple building blocks allow us to create actuators that convert energy from a variety of sources (such as chemical, electrical and heat) into mechanical energy. In this review we will discuss the advantages and potential pitfalls of using block copolymers to create actuators, putting emphasis on the ways in which these materials can be synthesised and processed. Particular attention will be given to the theoretical background of microphase separation and how the phase diagram can be used during the design process of actuators. Different types of actuation will be discussed throughout.

Keywords: microphase separation; block copolymer; actuators; physical gels; non-covalent interactions

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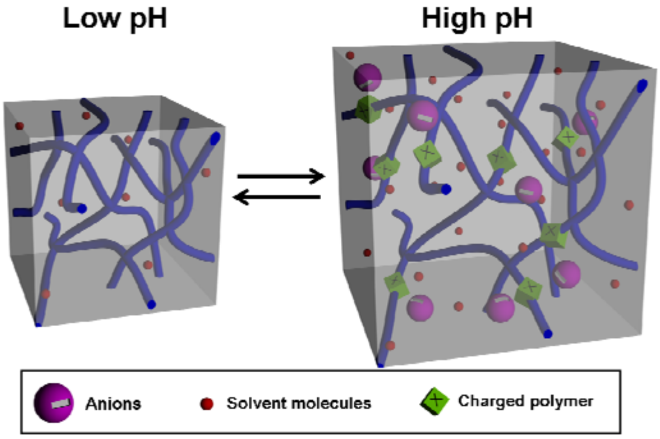
1. Introduction

Actuators are devices that convert the local energy of their surroundings (be it light, heat, electrical or chemical energy) into mechanical motion. A classic example of chemical actuation can be found in mammalian muscle whereby the contraction of muscle fibres is controlled by the "motor-protein" myosin. Its source of fuel (the external stimulus) is provided in the form of adenosine triphosphate

(ATP), which causes a conformational change in the myosin head groups, pulling them along actin filaments [1]. In short, chemical fuel is efficiently consumed to generate macroscopic motion. Emulating the general behaviour of these molecular machines is a rapidly developing area of research. In the polymer field numerous examples of actuators can be found in the literature. They can be designed to respond to a range of different thermodynamic properties; this change takes the form of an abrupt volume transition. A plethora of different applications have been demonstrated which take advantage of such a transition. Examples include drug delivery/therapeutic systems [2-4], "lab-on-chip" production [5] and synthetic muscle analogues [6-9].

An example of a "muscle type" volume transition taking place within a polymer network is shown in figure 1. This material is able to transduce an external stimulus (in this example a pH change) to drive an influx/ expulsion of solvent molecules and ions, causing a mechanical response in the form of a macroscopic volume change in the gel. In this example, the external stimulus is driving a three-dimensional swelling/collapse. However it should be noted that in nature muscle actuation is typically anisotropic. The conformation change in the muscle filaments produces a unidirectional change in length to perform work [10].

Figure 1. Illustration of a volume transition in a cross-linked polybase network triggered by a pH change.

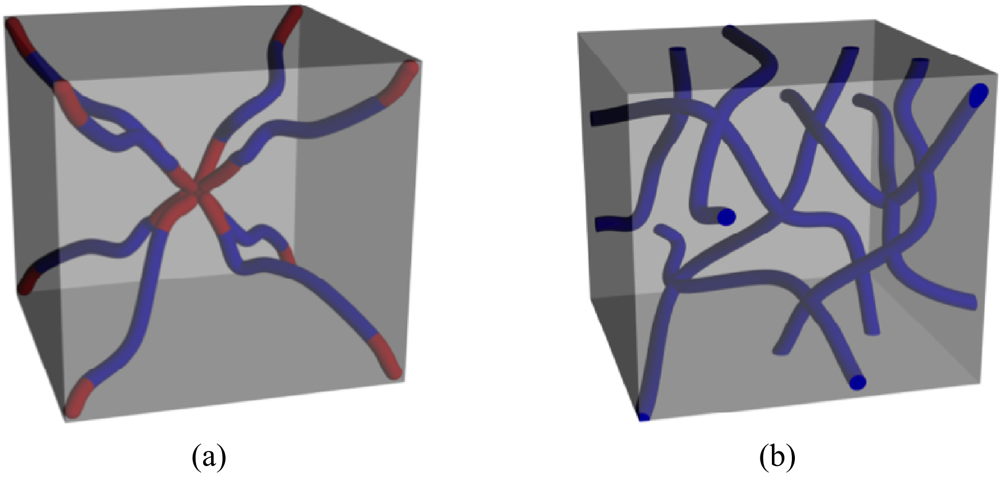


In biological systems such as protein motors, the actuation is driven by motion at the molecular level. Conformational changes that occur at this length scale lead to an overall macroscopic shape change. A number of key features associated with molecular machines are attractive to researchers. Most pertinently, perhaps, is their (1) controllable amplitudes (which may be large), and (2) controllable directional motion. This review will focus on recent strategies employed by researchers to synthesise and optimise novel responsive actuators, based on supramolecular block copolymers that operate with characteristics similar to molecular machines.

2. Stimuli-Responsive Polymer Gels

A hydrogel is composed of a three dimensional network of polymer chains held together by cross-links, and is capable of accommodating a large volume of water. They are typically referred to as either physical or chemical gels, which relates to the type of cross-linking holding the network together. In the case of chemical gels, they are cross-linked through covalent bonds. Physical gels, on the other hand, contain non-covalent cross-links. The latter can be formed through several routes including microphase separation [11-13], hydrogen bonding [14,15], peptide-peptide interactions [16] and ionic cluster interactions [17]. A simplified illustration of the two network types is shown in figure 2. The cross-links play an important role; they provide structural integrity. Without them the material would simply dissolve (or become dispersed) if it were placed into a good solvent for the polymer. The type, distribution and quantity of cross-linking define the final properties of the gel [18] and ultimately its end application.

Figure 2. Schematic illustrations of **(a)** a physical gel created through non-covalent bonding and **(b)** a chemical gel created by chemical cross-linking. Note: the red domains in (a) represent the aggregated domains.



Hydrogels are well known for their large volume changes in response to external conditions [19]; a property which is controlled by a delicate balance between hydrophobic and hydrophilic forces. These changes were exploited by researchers over fifty years ago to create synthetic “muscle-like” actuators. Kuhn and Katchalsky [7] were the first investigators to report the coupling of chemical change and mechanical response of polyelectrolytes. In these gels volume changes were driven through changes in the ionisation state of the gel, and integrity of the gel was maintained through chemical cross-links. For applications which mimic “muscle-like” behaviour it is important to ensure that the materials are mechanically robust, as well as being able to respond to external conditions with high response rates. It is not enough that a material demonstrates a simple actuation.

For hydrogel actuators (derived from bulk gels) which are driven by the transport of solvent molecules and ions into and out of the network (such as pH or temperature-responsive gels) the response rate is related to the thickness of the material. Studies have shown that their response rate is controlled by the diffusion-limited transport of components within the gel. This rate limiting process is inversely proportional to the thickness of the smallest dimension of the gel [19,20].

To overcome the inherent problems associated with slow response rates in hydrogels researchers have sought to reduce the overall dimensions of the gel (the thickness of the smallest dimension). One of the first examples of miniaturisation was demonstrated by Beebe *et al.* [21] who, through the use of lithography, created micron-sized chemically cross-linked hydrogel components inside micro-fluidic devices. These were confirmed to show greatly improved response rates. Another strategy that has been predicted [22] and demonstrated [23] to increase the response rates is focussed on processing nano and micro-fibres. Nanofibres have a greatly increased surface area compared to a monolithic gel of the same material and this increases the response of the gel.

3. Top-down *versus* Bottom-up

In the work by Beebe *et al.* [21] the devices were created using a so called "top-down" approach. A macroscopic cross-linked hydrogel, was synthesised by photopatterning to create the final device with the required shape and size. One of the disadvantages of this technique is that the final dimension of the material is limited to a minimum size of approximately 100 microns. This is due to the strong UV absorption within the photoresist [24]. As the wavelength of the lithography beam is reduced, energy is absorbed, heating the material rather than etching out the desired pattern. The top-down approach was used in this example because the gel was chemically cross-linked. Chemically cross-linked polymers are insoluble materials therefore the processing routes that are available are severely constrained. The macroscopic shape of the final material must be defined during the cross-linking procedure using moulds or afterwards using lithography techniques.

To overcome both the size limitations and the general lack of processability researchers have looked towards the use of block copolymers. This is mainly attributed to their inherent solubility (hence ease of processing) and promise of being able to define structure at molecular length scales. Block copolymers can be tailored using the concept of supramolecular chemistry to create devices which are greatly improved in their functionality and performance [25]. The proceeding section will discuss how supramolecular design principles based on the "bottom up" principles of nanotechnology can be used to create block copolymer derived actuators which show both controlled and directional actuation. For a more in depth discussion on the generalistic approach of bottom up construction towards the creation of molecular devices the authors are directed to the review of Belzani [26].

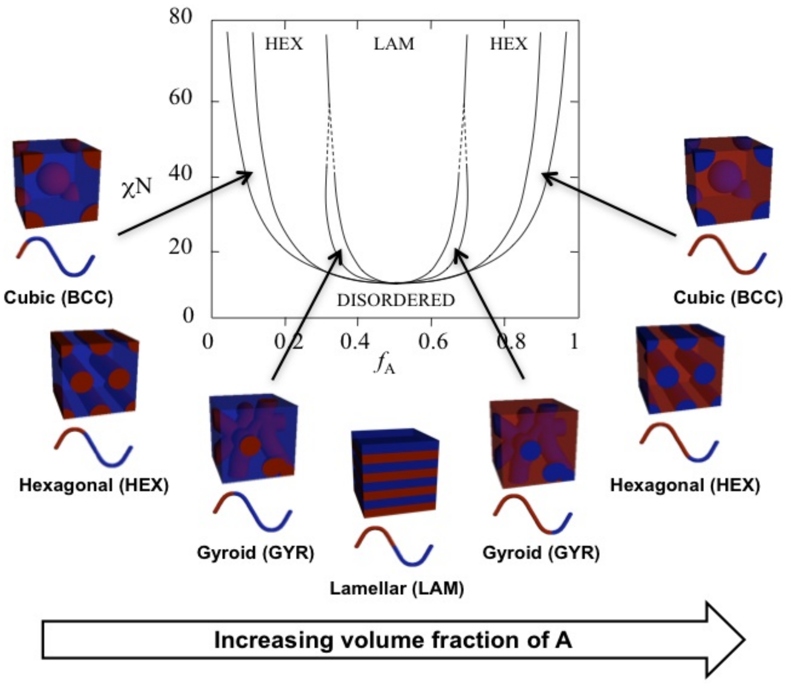
4. Supramolecular Actuators Derived from Block Copolymers: The Basics Design Elements

4.1. Microphase Separation in Block Copolymers

Block copolymers are macromolecules which contain two or more chemically different subunits covalently linked together [27]. One of the simplest forms of a block copolymer is a linear diblock where two distinct homopolymers are joined together in sequence (*i.e.*, A_xB_y). A variety of higher order block copolymer architectures can be synthesised, such as linear triblock copolymers which contain two different monomeric repeat units (—$A_xB_yA_z$—), or three distinct polymer chains in sequence (—$A_xB_yC_z$—). Structures may not necessarily be linear, for example, star copolymers can be synthesised when more than two distinct block copolymers are attached at a common branch point [28,29].

When two or more component blocks are chemically fixed together there is generally some degree of incompatibility [30]. It is now well understood that in order to minimise this incompatibility, block copolymers self-assemble into various structures as shown in figure 3. There are competing forces arising from the enthaplic contribution of mixing (or de-mixing) and the entropic penalty associated with elongating the polymer chains, where the structures adopted depend on the balance between these two factors. These structures have very well-defined spacing and size on the nanometre length scale [31-33]. This local reorganisation within block copolymers is known as *microphase separation*.

Figure 3. Theoretical phase diagram and corresponding morphologies for diblock copolymers. The phases are indicated as follows: body centred cubic (BCC), hexagonal cylinders (HEX), gyroid (GYR) and lamellar (LAM). f_A is the volume fraction of polymer block A, χ the Flory-Huggins interaction parameter and *N* the total degree of polymerisation. Adapted with permission from [33]. Copyright 1996 American Chemical Society.



In a two component block copolymer, regions rich in A and B are formed, the morphology of which is dominated by the internal interfacial energy, which stems from the incompatibility of the blocks [35]. Microphase separation is essentially an equilibrium process that represents a balance between thermodynamic and entropic forces. Thermodynamically it is driven by the enthalpy of demixing of the component blocks. During this process, macrophase separation would be preferential, but is not possible as the component blocks are chemically bound together [36]. The enthalpy of demixing is proportional to the Flory-Huggins segment-segment interaction parameter, χ, which is found to be inversely proportional to the temperature according to equation 1 [37].

$$\chi = \frac{A}{T} + B \tag{1}$$

The values *A* and *B* are system dependent constants and *T* is the temperature. There is also an entropic penalty associated with microphase separation which is related to chain stretching; the magnitude of which is dependent on the degree of polymerisation, *N*. Elongated, or stretched, polymer chains are more entropically disfavoured than randomly coiled geometries. Above a certain temperature the component blocks mix homogenously resulting in a disordered phase (DIS). As the temperature is lowered (the Flory-Huggins segment-segment interaction parameter increases) the blocks separate into ordered microstructures.

The particular structure adopted by a block copolymer depends on the following controllable parameters; (i) the Flory-Huggins interaction parameter χ, (ii) the overall degree of polymerisation, N, (iii) the volume fraction of the component blocks, f, and (iv) the particular polymer architecture. In the case of a multi-component A-B-C triblock, one must consider three interaction parameters and two composition variables, compared to one interaction parameter and one composition variable in a diblock copolymer. This complicates the phase behaviour and increases the number of observed phases [38].

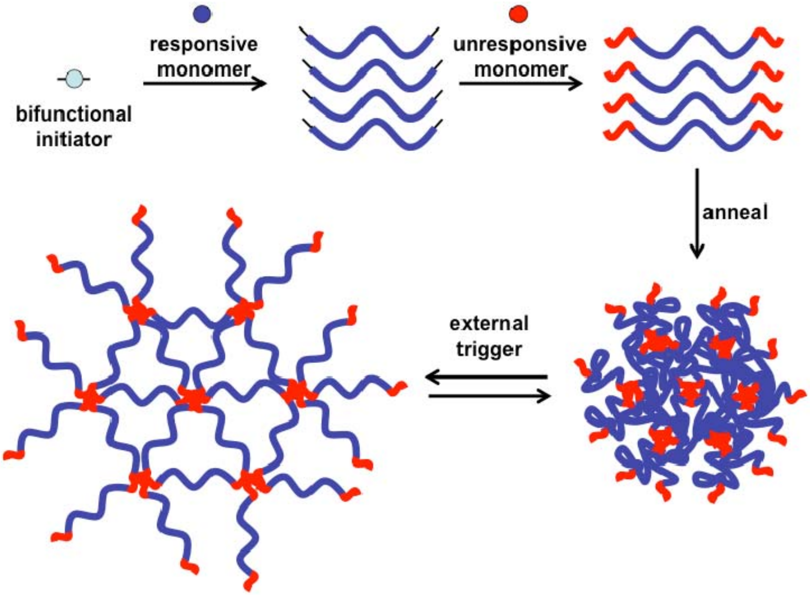
The nanoscale control offered using block copolymers can be used to create some unique devices. Through judicious choice of monomers, a range of materials can be created which are responsive to an assortment of stimuli. To get the most out of actuators based on physical network formation several design principles must be followed. Attention must be paid to every element including polymer architecture (diblock, triblock, star, *etc.*), phase structure (lamellar, cubic, *etc.*), the molecular weight, the molecular weight distribution, and processing conditions. One of the most common routes to create supramolecular actuators is through the use of A-B-A triblock copolymers, where the midblock (B) forms the largest overall component of the triblock. Typically, the midblock is the responsive component, and the end blocks (A) are usually non-polar. This material microphase separates, where the A blocks aggregate to form discrete domains interdispersed within a matrix of the responsive block [39]. This is illustrated in figure 2a, where the red segments physically aggregate to create junction points, also known as stickers. Such a formation of stickers is critical and strongly affects the final mechanical properties [40,41]. The largest and most successful applications of this principle is the use of thermoplastic elastomers [42]. A classic example is styrene-*block*-isoprene-*block*-styrene copolymers where glassy styrene micelles link the network together [43].

One of the greatest advantages of using a physical network is that it greatly increases the processability of the material [44]. In line with the bottom-up approach materials can be processed easily into various shapes and sizes and can be controlled at the molecular level to induce directional properties [45]. This is in contrast to chemically cross-linked gels which once formed can only be shaped by other methods such as lithography and laser micro-machining [45]. Physical gels are also unique because they can be dissolved and re-processed allowing for multiple use. Another advantage of physical gels, particularly those derived from self-assembled structures is that there is an increase in the cross-link uniformity compared to chemical gels [46]. This is clearly shown in figure 2. An increase in uniformity reduces the amount of network stresses when the polymer cycles through repeated volume changes and thus potentially increases both the mechanical strength and reusability of the material.

4.2. Synthetic Techniques

The phase diagram in figure 3 demonstrates the range of morphologies that are attainable using block copolymers (note: the figure represents a diblock copolymer but this can be used as a model for symmetrical triblock copolymers [39]). From this phase diagram it is possible to predict the approximate molecular weight and volume fraction required for a given morphology.

Figure 4. Schematic representation of the synthetic procedure and post-synthesis processing employed for the general preparation of a symmetrical triblock copolymer network using a bifunctional initiator.



The synthetic approaches which are used to create model networks are often based on controlled polymerisation techniques; examples include anionic [29,47,48], ring opening [49,50] and group transfer polymerisation (GTP) [51-53]. Symmetrical triblock copolymers synthesised using anionic polymerisation or GTP are typically derived from difunctional initiators. The initiator starts the reaction and is responsible for producing the living active centres, which go on to propagate to polymer chains. Difunctional initiators are the most common route to ABA networks as this simplifies the technique requiring only two sequential monomer additions, growing each monomer from both ends simultaneously. An example of the synthetic procedure is illustrated in figure 4. Using a monofunctional initiator would require three sequential monomer additions. This is disadvantageous as it increases the chances of introducing impurities which ultimately leads to the formation of dead ends and impure samples. Moreover, the approach reduces the probability of producing highly symmetrical macromolecules. When performed correctly, these techniques allow materials to be synthesised with very precise architecture, accurate overall molecular weight, and narrow molecular weight distributions (polydispersities typically below 1.2). Although these synthetic techniques allow a high degree of control over the polymer properties, they have the disadvantage that they are often laborious, time consuming and difficult to scale up. The reactions have high sensitivity towards impurities, such as water, and therefore rigorous purification of reagents is necessary.

The use of simpler techniques such as atom transfer radical polymerisation (ATRP) [54,55] can be used to synthesise similar networks. However, this is not a true living reaction and, in comparison to anionic methods, often leads to materials with higher polydispersity, particularly when targeting higher molecular weights [56,57].

4.3. Examples of Actuators Based on the Concept of Supramolecular Design

The idea of using a self-assembled structure in the context of "muscle-like" actuator was suggested by De Gennes [58] several decades ago. This concept was first realised by Li *et al.* who created a temperature responsive actuator based on an R-N-R lamellar phase separated nematic liquid crystalline triblock copolymer [59], where N represents a nematic polymer and R is a conventional rubber block (see table 1). Reversible changes in the material were driven by a nematic-to-isotropic phase transition, and the associated stretched to spherical shape change (around 20%) in the polymer chains. In this material the phase-separated domains were stabilised by chemically cross-linking the R end blocks. Ahir *et al.* have synthesised a similar nematic triblock copolymer, however they cross-linked the material through aggregation of end blocks made from terphenyl moieties [60]. Table 1 lists a number of different microphase separated polymers that demonstrate actuator like properties.

Table 1. Range of polymer actuators with their respective structural architecture, responsive nature and specific stimulus value.

Polymer name	Response stimulus and trigger value	Network orientation	Ref.
PMMA-*block*-PMAA-*block*-PMMA	pH, 5.5	Spherical—"Liquid Like"	[61,62]
PMMA-*block*-PDEA-*block*-PMMA	pH, 4–4.5	Spherical—"Liquid like"	[63]
PS-*block*-P2VP-*block*-PS	pH, 4–4.5	Rod	[64]
R-N-R[a]	Temperature[b] Voltage[b]	Lamellar	[59]
PS-*block*-PNIPAM-*block*-PS	Temperature, 32 °C	Lamellar, gyroid and cubic	[65]

[a] R = Poly(n-butyl acrylate)-co-poly(2-hydroxyethyl acrylate), (N)–LC homopolymer. [b] The material shows a progressive macroscopic shape change between 20 °C to 140 °C. The voltage value is unreported. PMMA = poly(methyl methacrylate), PDEA = poly[2-(diethylamino)ethyl methacrylate], P2VP = poly(2-vinylpyridine) and PNIPAM = poly(N-isopropylacrylamide).

Further developments in the use of phase separated systems were explored by Ryan *et al.* [62]. They synthesised a pH responsive A-B-A triblock copolymer, where A represents poly(methyl methacrylate) (PMMA) and B represents poly(methacrylic acid) (PMAA). By varying the length of the component blocks they created a material which after processing had a spherical microphase structure. The processed material was coupled with a Landolt pH-oscillating reaction. A Landolt reaction generates a bistable oscillating wave with a pH range between 3.1 and 7.0. When the pH oscillated above and below the apparent pK_a of PMAA it caused both a microscopic and macroscopic shape change in the material that was followed by both small angle x-ray scattering (SAXS) and video microscopy, respectively. Later work [61] on the same system focused on the strength of the material during cyclic pH changes. The material was found to have a peak power output of 20 mW kg^{-1}, a value which is far away in comparison to myosin at 20 kW kg^{-1} and striated muscle at 200 W kg^{-1} [61]. Following on from this work a similar A-B-A actuator was created with opposite polarity [63,66]. This was achieved by changing the midblock polymer to poly[2-(diethylamino)ethyl methacrylate] (PDEA). This polymer has the opposite pH response to PMAA and in contrast it swelled when placed at a pH below its apparent pK_a. The block length in this material was also tailored to ensure it had a spherical "liquid like" structure when processed. However, in contrast to the polyacid this material had poor mechanical properties and was prone to tearing and crack generation during cyclic oscillations. This was further demonstrated with another A-B-A actuator based on a different monomer pair, where A represent polystyrene (PS), and B represents poly(2-vinylpyridine) (P2VP) [64]. In contrast to the two previously mentioned systems this material had a rod-like microphase structure. The responsive P2VP network was held together by cylindrical pillars of PS, where two-dimensional swelling was thought to produce large stresses between grain boundaries. In this context the grain boundaries are defined as boundaries between areas of different alignment of the phase separated microstructure. This system was the weakest of all three and when placed into a cyclic reaction the material mechanically failed.

Researchers such as Li *et al.* [67] and Ahir *et al.* [60], alongside our group [63,64,66] have proven the fundamental use of microphase separated block copolymers for use as actuators. However there are clearly areas where further investigative studies are needed. To develop this area researchers have taken more systematic approaches to investigate how small changes in polymer structure affect the overall properties of the processed material. These modifications include molecular weight, molecular weight distribution and microphase structure. Each of these modifications will be discussed separately in the following sections.

4.4. Systematic Modifications to the Polymer Structure—Effect on Final Properties

4.4.1. Molecular Weight Distribution

The importance of narrow molecular weight distribution is particularly important in physical network formation where the glassy chain ends are used to create cross-linking domains. Tong *et al.* compared the mechanical properties of poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate)-*b*-poly(methyl methacrylate) triblocks prepared via both anionic polymerisation and ATRP. They found that triblock polymers formed via ATRP had much poorer mechanical properties. This was attributed to a larger polydispersity, where the smaller chains (present at a higher percentage in ATRP derived polymers) were unable to contribute to network formation resulting in loss of mechanical properties [45]. Polymers with larger polydispersities cover a wider area on the phase diagram, potentially spanning several preferred morphologies. This can cause a smearing effect of the final microstructure adopted. To ensure that only one morphology is adopted, polymers with a narrow weight distribution are especially targeted.

The requirement for an A-B-A network and its effect on mechanical priorities has also been investigated by Guice *et al.* [68] Here, they investigated the pH-response of self-assembled lamellar forming polystyrene–*block*-poly(2-hydroxyethyl methacrylate-*co*-2-(dimethylamino) ethyl methacrylate) diblock (PS-PHD) and triblock copolymers (PS-PHD-PS) containing varying amounts of 2-(dimethylamino)ethyl methacrylate (DMA). They established the polymer architecture played a critical role in the mechanical strength of the material. In PHD triblock copolymers the PS domains helped to serve as effective physical cross-linking points, but this was not the case in diblock material. In PHD diblock with high DMA content the material simply broke into pieces when protonated. Molecular analysis of the broken fragments (using SAXS) indicated that the polymer still retained a lamellar morphology. Therefore for the best mechanical properties the materials should be carefully synthesised to produce as near as mono-disperse sample as possible. Post-synthesis processing methods such as thermal and solvent annealing should also be carefully undertaken to minimise grain boundary imperfections.

4.4.2. Molecular Weight

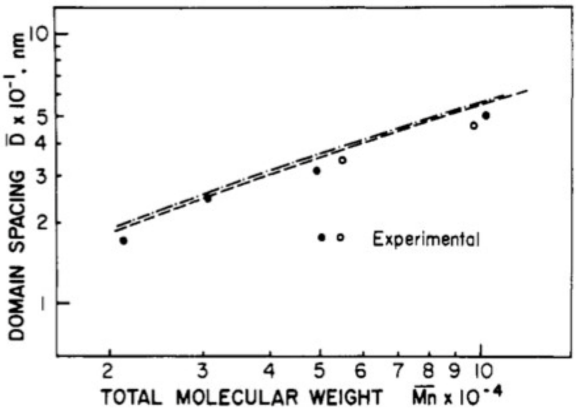
The molecular weight of the polymer is important for several reasons. There is a minimum critical molecular weight required for microphase separation to occur. For example, in a polystyrene-*block*-polybutadiene-*block*-polystyrene (S-B-S) triblock copolymer this value lies somewhere between 5000 gmol^{-1} to 10,000 gmol^{-1} [69]. In a well-defined block copolymer the molecular weight can be varied to increase or decrease the domain period of the network. The relationship between the domain spacing/period, *d* and the molecular weight (*N*) has been shown to increase systematically as a function of total molecular weight [34,70]. It follows an approximate scaling law as shown in equation 2.

$$d \propto N^{2/3} \tag{2}$$

The upper limit on the molecular weight is primarily defined by the type of polymerisation reaction. At higher molecular weights the amount of initiator must remain small which makes the polymerisation more challenging. Additional care must be taken to avoid chain termination, which can ultimately lead to materials with higher polydispersities.

This relationship between domain spacing and molecular weight is shown more clearly in figure 5. Hashimoto *et al.* [34] used SAXS to measure the change in domain spacing of a polystyrene-*block*-polyisoprene diblock copolymer as a function of its overall molecular weight. The data fits the scaling law predicted in equation 2. In practical applications this feature could be used to alter the amplitude of actuation.

Figure 5. Effect of overall molecular weight on the measured domain spacing of a polystyrene-block-isoprene diblock copolymer [34]. Adapted with permission from [34]. Copyright 1980 American Chemical Society.



4.4.3. Entanglement Molecular Weight

A feature closely related to the overall molecular weight is chain entanglement molecular weight, M_e. The entanglement molecular weight is defined as the molecular weight between each entanglement point. Entanglements arise due to the thermal motion of polymer chains which are able to overlap with each other along their primitive path, defined as the shortest distance connecting the two ends of the polymer together considering 'topological' constraints [71]. The entanglements act as virtual cross-links in a polymer sample, however, they are not to be confused with physical cross-links formed via self-assembly, which arise from microphase separation [72]. The value of M_e is specific for different monomer repeat units and can vary dramatically from polymer to polymer. In a physically cross-linked triblock both the micro domains (end block aggregates) and entanglements contribute towards the mechanical strength. Breakage of a material is characterised by ductile failure of the micro domains [73].

The major role of entanglements is to delay fracture of these glassy domains. Tong *et al.* investigated the effect of entanglement molecular weight by measuring the tensile strength of a series of PMMA-*block*-poly(alkyl acrylate)-*block*-PMMA, where the midblock was varied with alkyl groups of various lengths. In a plot of ultimate tensile strength *versus* $1/M_e$ for the central block they found a linear relationship. This was fitted using linear regression, giving the equation as shown in equation 3.

$$F = 9.5 + 1.45 \times 10^5/M_e \tag{3}$$

This relationship highlights that it is important to choose a monomer with a low entanglement molecular weight to get the best mechanical performance. However, in the design stage getting the correct combination of material priorities and mechanical properties may not always be possible. For example, it may be possible to source a monomer that has the desired response characteristics (*i.e.*, has a volume transition at a specific pH) but may only have a low entanglement molecular weight. This issue in many circumstances will restrict the usability of a large range of monomers.

4.4.4. Phase Structure

It is also important to consider how the microphase structure changes the polymer properties. Nykaenen *et al.* [65] have demonstrated this effect. They synthesised a number of temperature responsive polystyrene-*block*-poly(N-isopropylacrylamide)-*block*-polystyrene triblock copolymers. They compared the swelling ratio of the hydrogel as a function of its microphase morphology and found this to have a large effect. Hydrogels with a spherical morphology were found to have the largest swelling ratio, and those with lamellar the smallest, as expected. This was a result of the lamellae domains hindering the diffusion of water, in combination with a large number of grain boundaries (due to the domains being misaligned) effectively locking in the responsive units, compared to the spherical morphology that did not restrict expansion in any direction. To ensure a system has the largest three-dimensional volume transition it is therefore necessary to target a cubic morphology. For muscle mimicry, however, where a unidirectional response is sought, a lamellae-structure may be favoured.

5. Conclusion

This review has shown that block copolymers have proven applications in the area of actuation. Miniaturisation and the corresponding increase in response rate was the first step used by researchers to increase their practicality as actuators. “Bottom-up” manufacture was the next step and clearly a great deal of information can be programmed into the materials at the design stage. Compared to the “top-down” approach the materials can now be designed with a much higher degree of control bringing them closer to the more sophisticated analogues in nature. However, we are far away from this. It is clear that there is still much to be learnt in this area. There are many variables we can change with block copolymers, many of which have been discussed throughout the review. The nature of the monomers, the molecular weight and molecular weight distribution are all properties that must be considered when designing a new material. Ultimately, the most appropriate material may not be practically obtainable as the synthesis of these highly defined networks requires quite often time consuming and meticulous synthesis. The best material may ultimately be a compromise. However with continuous developments in synthetic methodology the material toolbox from which we create our smart devices is ever-expanding.

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