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Stereochemical enhancement of polymer properties

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Abstract

The importance of stereochemistry to the function of molecules is generally well understood. However, to date, control over stereochemistry and its potential to influence properties of the resulting polymers are, as yet, not fully realised. This review focuses on the state-of-the-art with respect to how stereochemistry in polymers has been used to influence and control their physical and mechanical properties as well as begin to control their function. A brief overview of the synthetic methodology by which to access these materials is included, with the main focus directed towards stereochemical control over properties such as mechanical, biodegradation and conductivity. Additionally, the advances being made towards enantioseparation, enantioselective catalyst supports and stereo-directed transitions are discussed. Finally, we also consider the opportunities that the rich stereochemistry of sustainably-sourced monomers could offer in this field. Where possible, parallels and general design principles are drawn together to identify opportunities and limitations that these approaches may present in their effects on materials properties, performance and function.

Introduction

Nature has evolved the ability to create large and complex molecules in which the precise control over both the sequence and spatial arrangement of the atoms is critical to their performance. The 3-dimensional topological control over the arrangement of bonds is as important to the function and behaviour of molecules as any other factor, and is critical to the structure-function relationships that occur within biological systems. While the effect of stereochemistry on functionality is probably best known in the examples of small molecule drugs such as thalidomide (one enantiomer is effective against morning sickness, the other is teratogenic) or naproxen (one enantiomer is used to treat arthritis pain, the other causes liver poisoning with no analgesic effect), it is also clearly represented in biopolymers where stereochemistry has pronounced effects on structure and hence function. For example, DNA, which is at the heart of all biological systems, requires the chirality of the deoxyribose sugar in its backbone to ensure that the double helical structure can form by supramolecular interaction between the complementary nucleobase residues that are attached to them. Furthermore, the simple stereochemical difference between natural rubber and gutta-percha (the *cis-* and *trans-*isomers of high molecular weight polyisoprene respectively) results in remarkable differences in their mechanical properties, with gutta-percha being a harder, more brittle and less elastic material than its isomer.

The distinct influence of the stereochemistry in biopolymers on their structure and hence performance makes it reasonable to expect such aspects of synthetic materials to be equally

important. Yet this area has received little study, partially a consequence of the challenges of creating large macromolecules with well-defined sequence and stereochemistry at each repeat unit. Clearly, creating materials with controlled stereochemistry in particular has the potential to result in novel materials with complex behaviour and function. While much of our knowledge in this area results from the significant advances over the last 70 years with polyolefins, this aspect of polymer design has significant room to grow given the rich stereochemistry of many sustainable or renewably-sourced monomer feedstocks and the increasing drive towards their use. This review article examines the work to date in which control over stereochemistry in the polymer has led to a notable change in thermal or mechanical properties, or has enabled the functional behaviour of the material to be manipulated. It will further consider areas and define opportunities in which stereochemistry could be used to enhance both the properties and function of the polymers and materials that result.

There are several ways that stereochemistry can be incorporated into polymers that influence the properties of materials that are formed from them (**Info Box 1**). Although definitions of stereochemistry in polymers can vary in some instances, for the purposes of this review, we have followed literature precedent[1,2] to the define different ways in which stereochemistry forms part of polymers as follows: main-chain stereochemistry is defined as polymers that contain stereochemistry within the backbone of the polymer; side-chain stereochemistry has been used as a term to define polymers in which the stereochemistry is not directly connected to the backbone and are largely excluded from this review on account of the minimal influence that the majority of these groups have on the behaviour of the resulting polymer. Main chain stereochemistry includes both cis/trans (geometric isomerism) (*i.e.* in polyisoprene), in which the planar rigidity of the double bond or ring unit leads to stereoisomerism, and optical stereoisomers in which a chiral centre sits on the polymer backbone (*i.e.* in polypropylene or polylactide) (of course, it remains possible to have more than one type of stereochemistry present in one polymer chain). Finally, even in cases where there is not clear chirality or stereochemistry in the polymer structure, atropisomerism can be directed to create right- and left-handed polymer helices (*i.e.* creating polymer stereochemistry). While this area has not been exhaustively reviewed on account of other articles that adequately cover that area, some discussion of this potentially important area has been included and focuses on the use of monomers with additional chiral groups.

Info Box 1. Stereochemistry definitions

Tacticity describes the relation between adjacent stereocentres using the Bovey formalisation where i = iso (same) and s = syndio (different). The relation between two stereocentres is referred to as a diad, three stereocentres, triad, four – tetrad and so on. The distance that tacticity in polymers can be detected varies depending on the polymer structure.
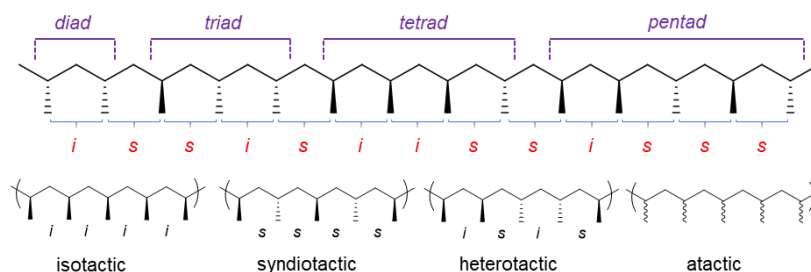
A polymer **stereocomplex** is a stereoselective interaction between two complementing stereoregular polymers, that interlock and form a new composite, demonstrating altered physical properties in comparison to the parent polymer. Typically these are polymers with different stereoregular structures such as isotactic and syndiotactic poly(methyl methacrylate) or poly(L-lactide) and poly(D-lactide).

Main-Chain Stereochemistry: Optical Stereoisomerism

Vinyl Polymers

The importance of stereochemistry in polymeric structures has been recognised for decades since the first report discussing structural differences of poly(vinyl ethers).[3] Initial developments in polymer stereochemistry focussed on the ubiquitous class of plastics known as vinyl polymers, with some of the most notable achievements being the synthesis of isotactic forms of polypropylene (PP)[4], polystyrene (PS)[5], and poly(methyl methacrylate) (PMMA).[6] Soon after these findings, a massive undertaking was initiated to improve the synthetic methods to modulate the stereochemistry in such materials and to access other stereo-controlled architectures. Presently, state-of-the-art methods for stereo-controlled vinyl polymerisations generally feature single-site transition metal catalysts.[7] The stereochemistry in polymers produced from well-defined metal catalysts can be dictated by enantiomorphic site control (chirality of the catalyst face) or chain end control (chirality of the end group), and there are many reviews outlining the general synthetic mechanisms for such stereospecific α-olefin polymerisations.[8-13] Instead, this section will focus on how stereochemistry affects bulk material properties. In order to illustrate the importance of stereochemistry on polymer properties, exemplary classes of vinyl polymers (PP, PS, and PMMA) will be examined. One of the most prominent factors affecting thermomechanical properties is the crystallinity of the sample (**Figure 1**). In turn, crystallinity can be thought of as an indication of order at the molecular level and such order is heavily dependent upon the relative orientation of the side-chain substituents (tacticity) along the polymer chain. Thus, this concept will be extremely critical to the following discussion.
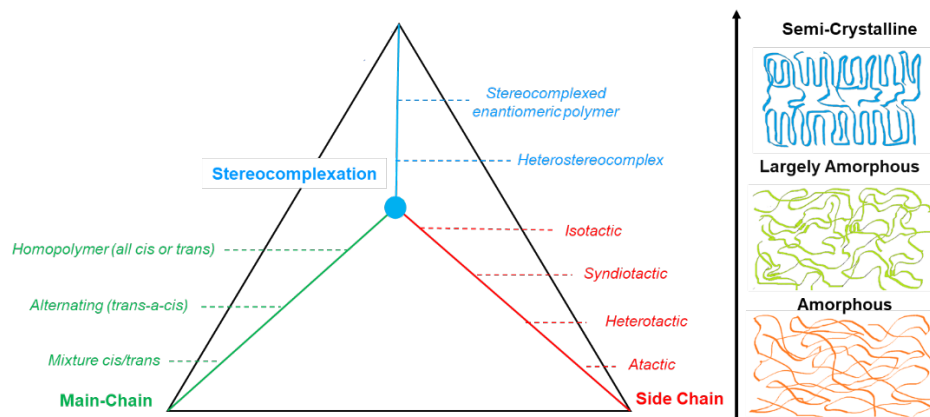
Figure 1. Schematic representation of relationship between polymer stereochemistry and crystallinity.

PP is perhaps the most well studied of the vinyl polymers and the properties are largely dependent on tacticity. The thermal properties – *e.g.* glass transition (T_g) and melt temperature (T_m) – of atactic polypropylene (aPP) and isotactic polypropylene (iPP) vary considerably, with the different isomers additionally displaying divergent mechanical properties. While aPP is a soft, rubbery and amorphous in nature, iPP is a hard thermoplastic with a distinct melt transition (T_m ~ 160 °C) as a consequence of ordered chain packing between the polymer chains. Perhaps most importantly, neither stereopure iPP or aPP homopolymers are commonly used as a result of their undesirable mechanical properties. Instead, a formulation of PP having some degree of stereo-regularity and stereo-irregularity produces a material with superior mechanical properties. Natta was the first to produce and characterise PP that contained both isotactic (crystalline) and atactic (amorphous) segments resulting in a material possessing high tensile strength and elasticity and today these materials are known as thermoplastic elastomers (TPE), (**Figure 2a**).[14] Subsequent efforts focussed on rational tuning of the relative ratio or placement of stereo-blocks (isotactic *versus* atactic regions) in order to improve mechanical properties.[15-20] It is worth mentioning that syndiotactic PP (sPP) (first synthesised by Natta[21] in 1962) has significant crystallinity, but is not as mechanically robust as the isotactic analogue as a consequence of its unique morphology that is characterised by disorder and large fractures within the crystal lattice.[22-24] Nevertheless, the tailoring of important properties, such as melt viscoelasticity, is possible by synthesising structures with amorphous regions interspersed between sPP domains.[25] An important lesson from studying polypropylene reveals that crystallinity is a significant component in determining the properties of a material, but it alone cannot be used to fully predict properties such as toughness, strength and/or elasticity. Hence, other factors need to be considered when seeking to design materials with enhanced thermomechanical properties.
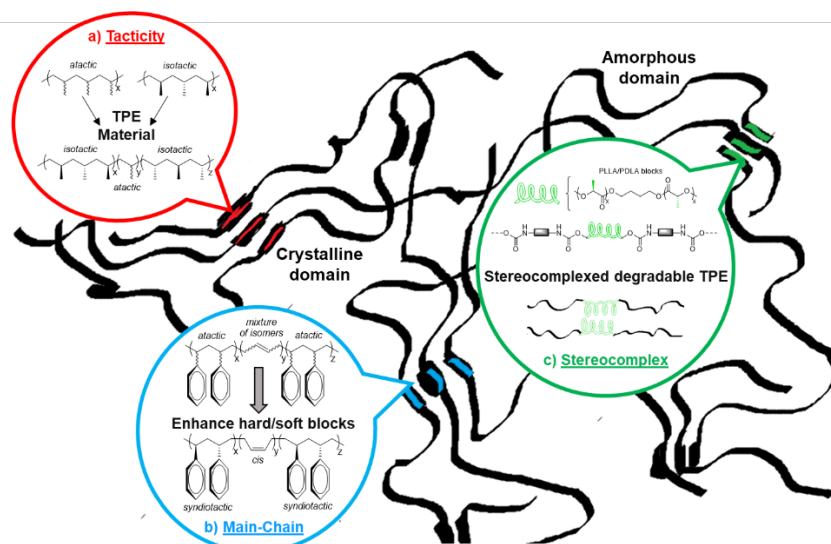
Figure 2. Examples of how stereochemistry can influence the mechanical properties of thermoplastic elastomers.

PS is one of the oldest yet most important industrial plastics. Before Natta's discovery of isotactic PS (iPS) in 1960[5] it was known only in an amorphous, atactic (aPS) form. There is little difference in most thermal properties (*e.g.* T_g and heat capacity (ΔC_p)) between the atactic and isotactic PS polymers, but iPS is capable of crystallising upon annealing (60% crystallinity, T_m ~ 250 °C). This imbues the material with improved mechanical properties relative to its disordered, glassy analogue, especially at temperatures greater than their respective T_g's (*c.a.* 100 °C). However, iPS has found little commercial use as the crystallisation process is too slow for industrial processing techniques.[26] Conversely, syndiotactic PS (sPS) was serendipitously produced in 1986 and found to be markedly different from the isotactic version.[27] The equilibrium melt temperature of sPS is approximately 50 °C greater than iPS.[28] sPS also has the added advantage that it can crystallise at an appreciable rate, approximately an order of magnitude faster than iPS, largely relegating iPS to academic investigations.[29,30] The thermal stability of sPS (and iPS) are greater compared to the atactic variant, indicating that stereochemistry can also influence thermal degradation profiles.[31] Furthermore, while sPS retains the attractive characteristics of aPS such as mouldability, excellent electrical properties, and resilience to hydrolytic degradation, it is more viable in manufacturing operations (*e.g.* injection moulding or extrusion) because of its rapid crystallisation.[32] Finally, sPS is a more robust material because the entanglement molecular weight (M_e) is approximately half of the value for iPS due to higher rotational energy barriers of the phenyl groups.[33] Another interesting polymer of sPS is the stereoblock sPS-*b*-aPS architecture that exhibits thermal properties dependent upon sPS content, *i.e.* the T_m and crystallisation rates increase as a function of sPS content.[34,35] Substituted analogues of PS, such as poly(α-methylstyrene), also display improved properties for syndiotactic-rich samples such as higher decomposition temperatures and T_g's.[36] The syndiotactic form of PS is the most interesting in terms of material properties, which contrasts the characterisation that syndiotactic PP is less robust than its isotactic counterpart even though both have similar degrees of crystallinity. The examination of PS tacticity demonstrates another important concept in polymer stereochemistry; generalisations about polymer stereochemistry must be made with extreme caution since subtle perturbations can yield divergent properties. Furthermore, by tuning polymer stereochemistry, the mechanical properties of a polymer can be greatly enhanced to produce a useful material. Specifically, while aPS has very poor mechanical properties, sPS is a tough thermoplastic with mechanical properties comparable to some Nylons.

Even though all carbon-based vinyl polymers have garnered significant attention over the past decades, polar vinyl polymers (*e.g.* acrylics) have also become ubiquitous due to advances in catalyst development.[37] The stereochemistry of PMMA in syndiotactic (sPMMA) and isotactic (iPMMA) forms was discovered contemporaneously with Natta's findings on polyolefins.[6] Dissimilar to the stereochemical trends observed in most nonpolar vinyl polymers, the stereochemistry of PMMA has a very noticeable effect on thermal transitions between syndiotactic and isotactic analogues ($\Delta T_g >$ 70 °C).[38-40] Even though iPMMA softens at a much lower temperature than sPMMA, the former is able to crystallise while the latter is amorphous and behaves similarly to atactic PMMA (aPMMA). Stark differences between dynamic mechanical properties also exist with relaxation processes occurring at lower temperatures in isotactic polymers.[41,42] It has been suggested these peculiar features of the isotactic version are due the adoption of a helical confirmation, something that is not observed for sPMMA or aPMMA.[42] Apart from thermal and mechanical properties, other bulk material properties also display stereochemical effects. For example, gas permeation properties[43] and chemical degradation rates[44,45] are very sensitive to stereochemistry. The most obvious attribute for acrylics and other vinyl polymers is the vast array of potential derivatives owing to their ease of functionalisation and consistent polymerisation chemistry. A recent example of a vinyl polymer with carbazole side-chain units (a nonconjugated electroactive polymer) displayed a positive correlation between conductivity and isotacticity.[46] Nevertheless, many stereo-controlled vinyl polymers are simply unknown. This is mostly due to the fact that state-of-the-art stereoselective synthetic methods are often not amenable to functionally diverse monomers due to either steric constraints and/or functional group tolerance of the catalyst. A recent report that features an innovative stereo-controlled synthesis to produce isotactic polyvinyl ethers with robust thermomechanical properties is particularly encouraging.[47] Still, relating stereochemistry to material properties has yet to be fully explored and continued improvement of synthetic protocols are vital to achieving this.

Vinyl polymers are arguably the most significant class of materials with over three hundred formulations that are available commercially, featuring a range of tailored thermomechanical properties.[48] Unsurprisingly, numerous critical concepts in polymer stereochemistry were refined by studying these materials. Although there are still opportunities to innovate, the most important advancements will likely come from applying these lessons to emerging polymer classes. Specifically, the fate of waste vinyl polymer plastics is of high importance worldwide and biodegradable materials from renewable sources are likely to become the dominant commodity polymers. In order to improve the properties of renewable polymers to compete with vinyl plastics, stereochemistry must be rationally leveraged. A recent example involving the stereoselective polymerization of a bio-sourced polar vinyl monomer, α-methylene-γ-butyrolactone (MBL), furnished a renewable polymer with thermal properties superior to petroleum-based plastics such as PMMA.[49]

Degradable polymers

Degradable polymers, natural polymers as well as modern synthetic polymers derived from sustainably sourced monomers, form the basis for a new generation of sustainable, eco-efficient plastics.[50-53] Presently, industrially-produced synthetic polymers are sourced from petroleum, currently heavily depleted by our increasing energy demand[54] and a large contributor to environmental waste concerns and greenhouse gases.[55,56] Thus, the use of renewable, biomass-sourced and biodegradable materials is considered to be an interesting route by which to replace petrochemical counterparts and is a long standing academic and industrial challenge in which several polymers, typically containing stereochemistry (**Figure 3**), have been developed. To be ultimately successful, the manufacturing processes of these polymers must become more cost-effective, their specific-target performance must match or even exceed the current standards, and

their end-of-use options must be quite diverse.[50] Leveraging stereochemistry will certainly be a crucial factor in the development of this relatively nascent technology.
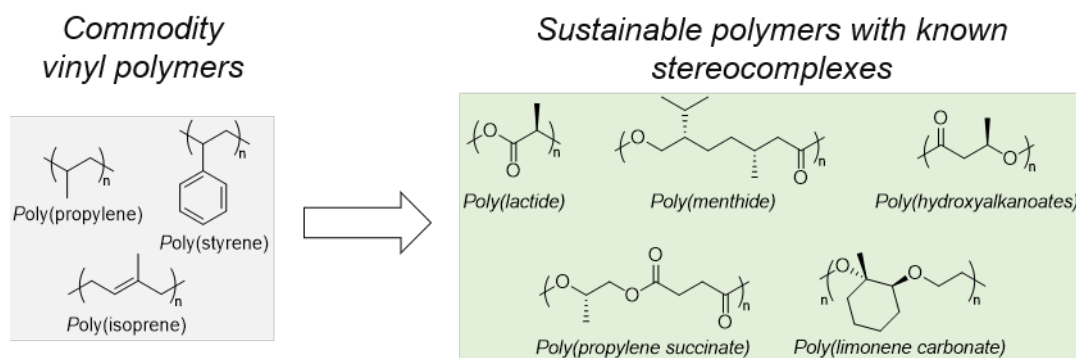

Figure 3. Degradable polymers with defined stereochemistry as replacements to vinyl polymers.

The most widely known sustainably-sourced polymer is polylactide (PLA).[57-59] It is renowned for its renewability, biocompatibility[60] and biodegradability.[61] It has garnered a significant amount of interest in both academic and industrial research for everything from packaging to biomedical applications.[62,63] PLA is most commonly produced through the fermentation of starch to lactic acid, followed by the synthesis of the cyclic ester monomer lactide (LA) and its subsequent ring-opening polymerisation (ROP). While PLA can also be prepared by step-growth polycondensation of lactic acid, the chain-growth ROP yields a greater degree of control of the molecular mass, molecular mass distribution ($Đ_M$), stoichiometric control of composition as well as higher end-group fidelity compared to the polycondensation reactions.[64] Finally, the application of ROP techniques also enables more facile control over the order of insertion of monomers into the polymer chain based on respective stereochemistry.[65,66]

Poly(α-hydroxyacid)s are a particularly attractive class of polymer because of the presence of asymmetric carbon atoms in the backbone. Lactic acid (2-hydroxypropanoic acid) is the simplest α-hydroxy acid with a chiral carbon atom and it exists as two optical isomers. Lactide, the cyclic diester of lactic acid, therefore possesses two stereocentres and three distinct diastereoisomers: *(S,S)-* or L-, *(R,R)-* or D- and the optically inactive *meso*-lactide which contains one of each stereocentre. All isomers are commercially available as enantioenriched samples or as a racemic mixture (*rac*-lactide) of L-, and D-LA. In turn, a variety of microstructures (*e.g.* atactic, isotactic, heterotactic and syndiotactic) can be constructed from this basic set of monomers, with each one possessing unique physicochemical and thermomechanical properties as well as different degradation profiles.[65,67-69] Notably, in contrast to many vinyl polymers, the lactide monomer possesses inherent stereochemistry and the synthetic challenge to create stereoregular PLAs is different, although there are many similarities in catalyst design and mechanistic considerations.

The physical properties of PLA make it a useful alternative to more common petroleum-derived polymeric materials (especially PS, as a consequence of their similar thermo-mechanical properties) as well as being suitable for more specialised applications in the pharmaceutical, biomedical and microelectronics fields.[70] While most ROP protocols result in predominantly atactic PLA, an amorphous polymer of low value, heterotactic PLA is commonly reported. As a result of the lactide monomer possessing two stereocentres, it is common to form heterotactic PLA (*ht*-PLA) from the ROP of *rac*-LA in which the stereocentres doubly alternate (*i.e.* -SSRRSSRR-). These polymers are generally amorphous with a T_g of ~ 30 °C, thus further narrowing the range of potential applications.[68] While the stereoselective ROP of *meso*-lactide can also lead to *ht*-PLA, it can be more

usefully polymerised to syndiotactic PLA which is a semi-crystalline material with a T_m of ~ 150 °C, significantly lower than that of polylactides with higher side-chain stereoregularity.[65] Relatively few studies have focussed on the synthesis of this polymer and the full utility perhaps remains to be uncovered. Stereocontrolled ROP of the optically pure monomers (L-LA or D-LA) leads to isotactic semi-crystalline PLA polymers (*it*-PLA) where all the stereocentres are aligned and has a T_m of ~ 180 °C and a T_g near 50 °C. These isotactic polymers are referred to as poly(L-lactide) and poly(D-lactide), PLLA and PDLA respectively.[71] The thermal and mechanical properties are dependent on the molar mass and the percentage content of the minor enantiomeric unit in the final polymer chain (*via* epimerisation of the enantiopure monomer during ROP or from the incorporation of the *meso*-lactide units into the stereoregular PLLA/PDLA chain) thus deteriorating the properties of the final material.[65,72,73] The mechanical properties of these polymers follow a similar trend to the thermal behaviour and are clearly dependent on the stereochemical makeup of the polymer's backbone. Semicrystalline *it*-PLLA has an approximate tensile modulus of 4 GPa, tensile strength of ~70 MPa, flexural modulus of 5 GPa, flexural strength of 100 MPa, and an elongation at break of about 5%. Therefore, it is generally preferred over the amorphous polymer (tensile modulus 1.2 GPa, tensile strength 59 MPa, flexural strength 88 MPa) for applications that require stiffer materials.[57,74]

Despite the accessibility of PLA microstructures, the most interesting materials are stereocomplexed (**Info Box 1**) architectures which will be thoroughly discussed in a separate section. Even so, the semi-crystalline nature of isotactic PLA has made it an ideal candidate for crystallisation-driven self-assembly (CDSA) and many well-defined architectures have been produced using PLLA block copolymers.[75-80] Polylactide is currently the gold standard in the field of biorenewable polyesters, but other promising chiral biodegradable polymers are of interest. The unique properties – including biocompatibility, defined degradation under physiological conditions, and formation of non-toxic degradation products – make it very attractive. Expanding the use and capturing the market share from polyolefins and other vinyl polymers will require improvements to brittleness, thermal properties and stability.

Analogous to poly(α-hydroxyacids), poly(hydroxy alkanoates) are polyesters with chiral carbon atoms that are obtained from fermentation processes of various bacterial strains. Apart from the advantages associated with biorenewability and biodegradability, the final constitution of the polymer (*i.e.* specific functional group at the chiral centre) can be modulated according to the chemical feedstock available to the bacteria, thus making it a very versatile platform for targeted material properties.[81-83] Poly(β-hydroxybutyrate) (PHB) is the simplest and most studied analogue and provides an excellent representative material for its class. Biosynthesised PHB is very crystalline and optically active due to its isotactic homochirality.[84-86] Recently, perfectly isotactic PHB was synthesized for the first time from a racemic monomer mixture.[87] In some respects, the thermomechanical properties are similar to isotactic PP (*e.g.* T_m ~ 180 °C and high stiffness); however, it embrittles more rapidly as a consequence of its thermal properties. Since bio-sourced PHB is always isotactic (iPHB), access to PHB with alternate microstructures must be synthetically achieved, usually *via* ROP of racemic β-butyrolactone.[88,89] Alternatively, the physical blending of iPHB with synthetic amorphous atactic PHB (aPHB) has been investigated as a method to alter polymer properties. In such blends there is considerable melting point depression relative to bacteria sourced iPHB.[90,91] Not surprisingly, the elasticity can be significantly improved (~ 10 fold) but at the expense of toughness, and the degradation kinetics are accelerated in the blended samples.[92] Metal-catalysed ROP has also been utilised to access syndiotactic PHB (sPHB) from racemic monomer mixtures[66,93-98] and from varying the feed ratios of optically active β-butyrolactones.[99] For highly syndiotactic samples the T_g is comparable to isotactic PHB, but the T_m is much lower ($\Delta T_m > 100$ °C) and sPHB displays elastomeric properties.[94,99] Although there are a large number of structurally

similar polyhydroxyalkanoates only a limited number of examples have been synthesised directly. The role of stereochemistry and its effect on bulk properties has been overlooked since most are easily obtained as homochiral, biosourced polymers. Synthetically it is possible to produce other stereo-controlled polyhydroxyalkanoates with controlled alternating microstructures[100-102] that may yield promising new functional materials. Furthermore, there is interest in producing copolymers by combining PHB with other polyhydroxyalkanoates[103-110] or PLLA[104,111-116] in order to modulate material properties; however, the stereochemistry of PHB has only been controlled in a few cases.[109-111,115,116] Taking stereochemistry into consideration in such systems should afford many interesting opportunities for biomedical applications.[117] As an example, the degradation of polyhydroxyalkanoate microparticles was dependent on overall stereochemistry with more controlled release kinetics observed for stereoregular structures.[109]

Poly(propylene glycol) (PPG), poly(propylene carbonate) (PPC) and poly(cyclohexylene carbonate) (PCHC) are other common, biorenewable polymer classes that have exploitable stereochemistry.[118,119] While stereochemistry is the focus here, it must be noted that regiochemistry is important for PPG or PPC and this can modulate material properties. Transition metal catalysed stereoselective epoxide polymerisation and copolymerisation is well developed and has led to many useful architectures.[120-123] Stereopure PPG is a crystalline, yet rubbery, polyester that has been synthesised with many different catalysts.[124-131] Surprisingly, the T_g and T_m seem to be independent of stereochemistry[126,130-132] since both isotactic[131,133,134] and atactic[132] isomers are crystalline. Moreover, the stereochemistry of the PPG unit in triblock architectures of PPG-b-PEG-b-PPG copolymers has little effect on material properties.[135] In order to enhance the thermal properties of PPO it can be randomly copolymerised with CO_2 to yield PPC. Stereopure (atactic, isotactic, and syndio-enriched) PPC is a ductile thermoplastic that has been studied for some time.[136-141] However, thermal and mechanical data on the stereopure materials is noticeably lacking, except for one study that examined the effects of regioregularity in PPC and derivatives.[136] To date, one of the most interesting epoxide-based polymers is enantiopure poly(propylene succinate).[142] By mixing the two enantiopure isotactic polymers that display slow crystallisation kinetics, a stereocomplex was formed with a dramatic improvement in crystallisation rate and T_m. Isotactic PCHC is a brittle thermoplastic that has been prepared from a variety of catalytic protocols.[143-153] Due to its stereoregularity, it is highly crystalline (although there is no clear trend between % crystallinity and % ee of the polymer) with a T_m greater than atactic PCHC (though the reported melting values have varied greatly).[143-146] The only systematic study relating T_m to % ee showed a positive correlation (T_m = 234–267 °C) between the properties for samples ranging from 78–99% ee.[143] On the other hand, syndiotactic-enriched PCHC has been qualitatively described as 'amorphous' but no thermal data was reported.[154] Terpolymers with constituent units of CO_2, propylene oxide, and cyclohexylene oxide have been thoroughly characterised according to overall polymer composition, but stereochemical effects were not described.[147,149] Although PPG homopolymers are relatively uninteresting materials on their own, more promising copolymeric and terpolymeric materials with variable composition and stereodependent properties, in some cases, are known. The diversity of such complex architectures should galvanise further investigation of stereochemistry in more sophisticated degradable polycarbonates and polyesters.

Optically active conducting polymers with chiral side-chains

Polyacetylene was the first conducting polymer featuring a chiral side-chain;[155] however, the introduction of large side-chains to polyacetylene tends to disrupt the conjugative pathway along the polymer backbone making these materials unsuitable for applications involving organic semiconductors. Thus, attention eventually turned to other conjugated backbones such as
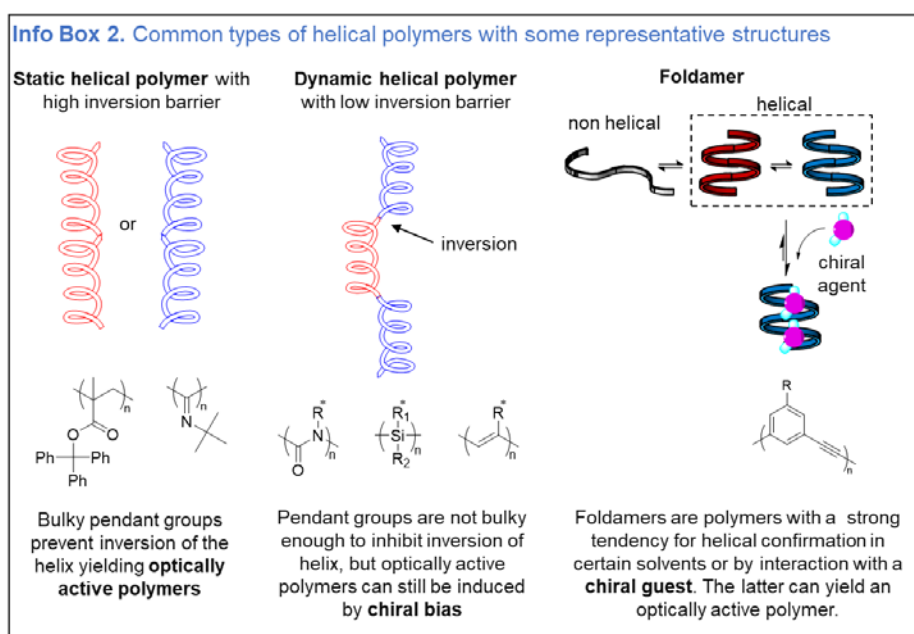
polythiophenes, polypyrroles and polyanilines since these polymers are easily functionalised and often retain conductivity even when bulky substituents are present.[156] Although conducting polymers are most recognisable in organic optoelectronics they also have great potential in sensing applications (*e.g.* bioelectronics)[157,158] due to their dynamic properties (*e.g.* electro-, solvato-, or thermo-chromism, and switchable redox chemistry) that can sometimes be amplified with chirality.[159,160] A good example of this enhancement is described for an organic thin-film transistor endowed with chiral side groups that showed improved responsiveness in sensing applications.[161] Furthermore, the conductivity and charge transport of conducting polymers in devices is intimately coupled to morphology[162-166] and chirality may be able to provide advantages in the form of increased solid-state ordering. Since the field of conducting polymers bearing chiral side groups is so expansive, only examples that specifically correlate bulk material properties to stereochemical effects or trends are highlighted. There are a few examples of conjugated polymers with main chain chirality, but the area is comparatively nascent and only one report (binaphthyl-containing polyfluorenes) features stereochemical-property relationships.[167] Moreover, conjugated chiral small molecules or oligomeric species often exhibit supramolecular self-assembly and form higher order macromolecular structures but these cases are beyond the scope of this review since they are not considered polymeric in nature.[168,169] Finally, optically active conducting polymers often possess distinct helicity and this characteristic is a major point of focus in many studies, but it will not be examined in this section.

When considering morphology, an optically active poly(azomethine) was shown to self-assemble into highly ordered fibrous structure while the racemic counterpart did not display any solid state ordering.[170] Similarly, more higher-ordered phases were observed in a polyacetlyene with a chiral side moiety than the non-chiral counterpart.[171] Polythiophenes with chiral thioether side-chains displayed morphological characteristics that correlated to the shape, size and sign of the CD signal by varying the processing conditions.[172] Chiral polyanilines, induced by the presence of a chiral counter-ion (D- or L-camphorsulfonic acid), have been utilised to create highly ordered conducting micro/nanofibers,[173-176] nanosheets[177] and "hexagonal superlattices" that mimic β-sheet protein structures.[178] Moreover, chiral poly(aryl acetylene) was manipulated into a variety of chiral nanostructures *via* metal complexation[179] and aromatic ester polymers were shown to form chiral nanoparticles.[180] The formation of such higher order structures is certainly influenced by the chiral nature of the polymers. In another example the electrochemical properties (oxidation and reduction potentials) of a chiral polypyrrole varied according to the stereochemical configuration of the side-chain.[181]

Benzotriazole-thiophene copolymers with chiral side-chains have been thoroughly investigated and compared to racemic analogues.[182] Although optical solid state properties were similar between the non-chiral and chiral polymers (apart from a chiral response from CD analysis), experiments that clearly investigate side-chain chirality in this manner are exceptional and it is refreshing to see. In a similar manner, another study examined benzothiadiazole copolymers by comparing the optically pure polymers to the racemic analogues.[183] For these polymers, X-ray scattering analysis revealed that the optically active polymers had more ordered morphologies due to tighter chain packing and this was corroborated by a red shift in the solid-state absorbance profile. Due to the simple fact that stereochemical influences differ between the studies, *i.e.* one polymer is affected by stereochemistry while the other is not, this should stimulate researchers to investigate such comparisons when it is possible.

Helical polymers

Helices are fascinating chiral objects that are ubiquitous in nature with the most illustrative examples being the double-stranded helix of DNA as the carrier of genetic information[184] and the ☐ helices in proteins.[185] Historically, the first synthetic helical polymer was characterised during Natta's investigations on polyolefins where he synthesised iPP and it was demonstrated to have a helical conformation in the solid-state.[4,186] However, this polymer was not capable of maintaining its conformation in solution, a recurrent challenge for the creation of helical polymers. Nevertheless, the current interest in helical polymers has recently increased with focus for applications in catalysis, chiral recognition, and the study of biological systems.[187,188] Chirality and optical activity can be inherent to helical polymers stemming from atropisomerism (steric hindrance related stereoisomerism) and they can be classified as having backbone stereochemistry while not having any chiral moieties in the backbone.[189-191] Additionally, significant attention has been devoted to the assembly of helical polymers into unique supramolecular structures, but that is also beyond the scope of this article (**Info Box 2**).[187]

Info Box 2. Common types of helical polymers with some representative structures

Static helical polymer with high inversion barrier

Dynamic helical polymer with low inversion barrier

Foldamer

non helical / helical

inversion

chiral agent

Bulky pendant groups prevent inversion of the helix yielding **optically active polymers**

Pendant groups are not bulky enough to inhibit inversion of helix, but optically active polymers can still be induced by **chiral bias**

Foldamers are polymers with a strong tendency for helical confirmation in certain solvents or by interaction with a **chiral guest**. The latter can yield an optically active polymer.

Polymer helices can be divided into two major groups depending on respective helix inversion energy. While in solution, most enantiopure polymers (such as aliphatic polyisocyanides, polyacetylenes, polysilanes and polyguanidines) have a low helix inversion energy and display fast helix inversion in solution, static helical polymers (such as polymethylmethacrylates/polymethylacrylamides and polyisocyanides bearing bulky aryl groups or poly(quinoxaline-2,3-diyl)s) have a high helix inversion energy and are conformationally stable structures, typically due to side-chain interactions (steric bulk). The copolymers of both type of helical polymers are remarkable because of the two major rules that govern their helicity: the "Sergeant-Soldiers"[192] and the Majority[193] rules. The "Sergeant-Soldier" rule permits the use of a very small amount of chiral units among achiral units to allow an optimal transfer of chirality while the Majority rule discards the obligation of utilising enantiopure monomers to attain high enantiomeric excess. Combined together, they open the road to the facile synthesis of high-purity chiral polymers from inexpensive components.

Perhaps the most obvious application for helical polymers is chiral recognition for enantio-discrimination (**Figure 4**).[187,194] In this area, they have been successfully developed for enantioselective adsorption[195,196] and enantioselective permeation (membranes).[197] For example, a hydrogel developed by imprinting chiral sites with helical polymers displayed prominent enantioselective adsorption behaviour.[198] Moreover, chiral recognition can be exploited in the case of static helical polymers such as polyisocyanide[196,199] and poly(triphenylmethyl methacrylate) (PTrMA)[200-202] which have also found utility as chiral stationary phases (CSPs) for HPLC columns. The dynamic and helical memory properties of polyacetylene have been leveraged for the same application but with the added advantage of a switchable chirality to potentially alter the elution order of the enantiomers.[203,204] Another interesting property of helical polymers is the amplification of optical activity from monomer to polymer, due to the synergistic effect with the helical backbone, as observed in metal-complexed helical polymers where an induced enantioselectivity was observed.[205,206] When applying this principle to dynamic helical polymers it is possible to produce an asymmetric catalyst with switchable enantioselectivity (**Figure 4**).[207] The enantioselectivity of organocatalysts can be improved[208-211] or even entirely induced[212,213] by the helical polymer scaffold. Utilising polymer helicity to effect enantioselectivity resembles a similar mechanism found in proteins containing α-helices and realises a step towards creating a synthetic enzyme.
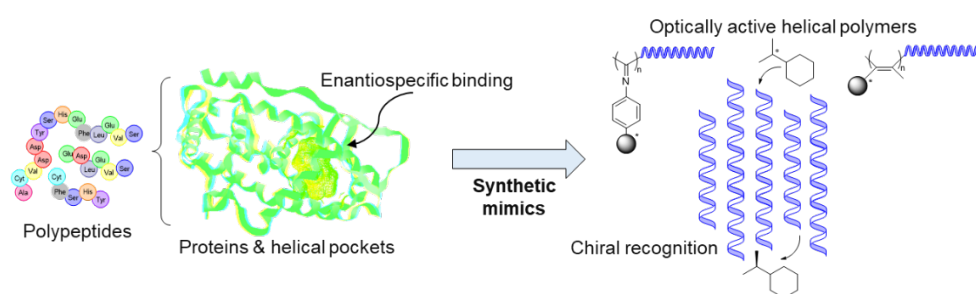
Figure 4. Synthetic helical polymers with biomimetic behaviour.

As a further example of the utility of stereopure chiral materials, a polyisocyanide containing peptide side-chains was developed as a biomimetic polymer gel displaying stress-stiffening responses comparable to biological tissue (**Figure 4**).[214] As a consequence of the ubiquity of helicity in naturally occurring polymers it is likely that synthetic variants will have a sizeable impact in the biomedical field, particularly in regenerative medicine. In addition to biomedical applications, polyisocyanates[215] and polysilanes[216] have been investigated in optical data storage devices due to their dynamic nature. It is theorised that the chiral information from the helicity (P and M) could be used as an analogue to the number based binary (0 and 1) used in current computing technology. Not only could this diversify the data storage/processing industries but it could also improve the renewability of future technological hardware. Finally, there has been renewed interest in higher order helical structures such as "helix-in-helix" superstructures[217] or the triple helical structure of stereocomplexed PMMA[189,190,218,219] which is a rare example of a multiple-stranded synthetic helix. Moreover, such structures have been implicated in "molecular sorting" based on the molecular weight of constituent polymer strands.[220,221] From a topological viewpoint, multi-stranded systems closely mimic natural helical assemblies such as RNA, DNA and certain proteins making them crucial to future nanomaterial development.

Main-Chain Stereochemistry: *Cis/Trans* Stereoisomerism

Polydienes

Similar to side-chain stereochemistry, the primary concepts of main-chain polymer stereochemistry were also developed from the study of polyolefins. Early discoveries focussed on characterising biosourced natural rubber (*cis*-polyisoprene or *c*PI) and gutta-percha (*trans*-polyisoprene or *t*PI). Although both polymers are commonly harvested as a latex from numerous tropical tree species,[222] synthetic variants can be synthesised from the direct polymerisation of isoprene. Similarly to other nonpolar vinyl monomers, the polymerisation of isoprene can proceed *via* radical, anionic, and cationic mechanisms; however, coordination-insertion polymerisation using metal catalysts (particularly organometallic lanthanides) has emerged as the preferred method since the microstructure can be controlled to mimic natural rubber, gutta-percha or compositions in between.[7,222-224] For example, recently developed protocols using lanthanide catalysts have yielded *cis/trans* stereoblock architectures.[225,226] Less commonly, isoprene can be polymerised *via* a 1,2 insertion mechanism to produce 1,2-polyisoprene featuring a pendant vinyl group.[227] However, further comment is not warranted since it is beyond the scope of this section (main-chain stereochemistry) and the side-chain stereochemistry for exemplary vinyl polymers has been previously covered. In the remainder of this section, stereochemistry will be correlated to bulk properties of the materials.

The *cis/trans* isomers of polyisoprene (*c*PI and *t*PI respectively) possess divergent properties that are dependent on main-chain stereochemistry. Examining the thermal properties, the T_g is similar between the isomers; however *t*PI has a much higher T_m than the *cis* variant (T_m *trans* = 89 °C and T_m *cis* = 34 °C).[223] It should be noted that the diblock architectures incorporating *trans*-1,4-polyisoprene segments display melt transitions according to DSC analysis[228,229] but similar polymers with *cis* segments are generally described as amorphous. These observations are corroborated when comparing the mechanical properties between the isomeric polymers. *c*PI is amorphous, soft, flexible and elastic whereas *t*PI is comparatively crystalline (existing in two dynamic ordered phases – α or β)[230] and tough.[231] This observation has been attributed to the better chain packing of the natural rubber unimers, though seemingly counterintuitive, compared to that of gutta-percha (**Figure 2**). Though the *cis* configuration of natural rubber imparts flexibility to the polymer chains, since they are randomly coiled at room temperature, when stretched the chains partially align which improve toughness. The polymer chains then return to their original coiled configuration when the stretching force is released and the sample returns to its original length, displaying a high degree of elasticity.[232] This strain-induced crystallisation of natural rubber is a self-reinforcing effect where crystallisation increases with increasing elongation and contributes to its high ultimate tensile strength.[222,233,234] Owing to its *cis* stereochemistry, natural rubber is more reactive and the physical and mechanical properties can be altered more easily than gutta-percha *via* numerous chemical modifications.[223,232] By vulcanising natural rubber the tensile strength becomes competitive with gutta-percha and the elongation at break still remains far superior.[223,235] Although biosourced PI is still industrially important, synthetic production using pure monomers provides better control of *cis/trans* ratios and it has been shown that the addition or impurities or additives (compounding with reinforcing fillers, *e.g.* carbon black and silica) can be controlled to target tailored mechanical properties.[236] Another industrially important substituted polydiene is polychloroprene (neoprene). Despite the structural similarity to polyisoprene, neoprene is produced exclusively with a *trans*-rich form (approximately 85% *trans*-, 10% *cis*- and 5% *vinyl*-chloroprene) with a similar main chain

structure to β-gutta-percha. Even with a high degree of crystallinity it has similar mechanical properties to natural rubber at room temperature as a consequence of a unique chain packing/repulsion interplay between the CH_2 and Cl moieties.[231] It should be noted that there is one report of *cis*-polychloroprene but it was synthesised *via* post-polymerisation modification and not thoroughly characterised.[237]

1,4-Polybutadiene (PB) is the unsubstituted analogue to PI and the absence of the methyl group yields a softer polymer and lower T_g affording a material with a wider operating temperature range than polyisoprene. PB (from 1,3-butadiene) was first synthesised in a stereo-controlled manner using Zeigler-Natta type catalysts (transition metal and lanthanide complexes) and metal based catalysts continue to remain useful today.[236,238] Anionic polymerisations were also found to be effective (and remain so) for stereoselective polymerisation where the *cis/trans* ratio can be tuned by the choice of solvent and/or organometallic initiator.[239] Different ratios of the three isomers (*cis, trans* and *vinyl*) of polybutadiene have a dramatic effect on both polymer properties and material performance and can be controlled by catalyst choice. As with 1,2-polyisoprene, *vinyl*-polybutadiene will not be covered here. PB with low *trans* content is easily processable, whereas with high *trans* content it is much harder to process at tolerable temperatures but has greater abrasion resistance.[240] One of the most important applications of PB is its incorporation into block copolymer architectures to afford high performance TPEs (**Figure 2**). The modulation of stereochemistry for polystyrene-polybutadiene (SB) based polymers is well described for both the PB segment (*cis/trans*) and styrenic section (tacticity), but full characterisation that seeks to relate material properties to microstructure and stereochemistry is often absent.[241] There are a number of reports on stereocontrolled SB based polymers that describe thermal properties, but these studies are particularly aimed at altering polymer properties according to microstructure and/or relative block length as opposed to changing the stereochemistry of the respective block(s).[229,242-248] Furthermore, a description of mechanical properties is missing for these systems. Nevertheless, there is one significant example to discuss that features of polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) with precise microstructure and stereochemistry (sPS and cPB). This material possessed a very defined phase separated morphology and superior thermal properties to the atactic analogue, but the PB stereochemistry remained unchanged and mechanical data is omitted.[245] Simultaneous tuning of stereochemistry in the main-chain and side-chain of block copolymer architectures should provide a plethora of interesting materials. However, there needs to be an effort to explicitly connect stereochemistry to bulk properties in order to design future materials more coherently.

Step-growth polymers containing unsaturated ethers, thio-ethers, and aza-ethers

After the introduction of click-chemistry to the polymer community by Kolb, Finn and Sharpless,[249] these methods have emerged as a powerful tool for both polymer synthesis and modification.[250-254] Within polymer chemistry, the thiol-ene/thiol-yne addition reactions in which thiols are added across unsaturated carbon-carbon bonds are handy. Three possible mechanistic pathways exist for the thiol-yne reaction: radical mediated (photo- or themo-initiated), transition metal catalysed, and Michael addition (nucleophilic addition) where only the latter two mechanisms readily provide a resultant unsaturated, monofunctionalised product.[251] Transition-metal based catalysts (*e.g.* Ru, Ir, Ni, Pd, Pt, Au and Zr) have been shown to produce stereoregular vinyl sulphides *via* a migratory insertion mechanism which has been successfully translated to polymer chemistry.[255,256] The nucleophilic addition pathway requires a base (*e.g.* tertiary amine or phosphine)[257,258] and allows isolation of the unsaturated product in good yields.[259,260] The stereochemistry of the resultant alkene

can be tuned by appropriate choice of catalyst, solvent polarity, substrate choice, sequential monomer addition and post-polymerisation UV irradiation.[256,258,261] As such, the nucleophilic mechanism remains the preferred synthetic method for creating stereochemically-defined polymers *via* this pathway.

The control over the double bond stereochemistry in thiol-yne addition step growth polymers has led to an interesting new class of elastomers that exhibit substantial stereochemistry-dependent properties. Here, high *cis*-content materials were confirmed to be crystalline according to small-angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC) analysis (80% *cis*, T_m = 80 °C)*.* Conversely, polymers with significant *trans* content (> 30%) were amorphous and had a lower T_g (ΔT_g = 20 °C). Most dramatically, high *cis* materials (80% *cis*) were very tough yet still ductile (ultimate tensile strength = 54.3 ± 6.5 MPa and elongation at break = 1495 ± 66%) while high *trans* materials (32% *cis*) were much softer (ultimate tensile strength = 2.8 ± 0.4 MPa and elongation at break = 2970 ± 137%). The dramatic differences in mechanical properties between isomers was rationalised to be caused by altered chain packing that was dependent on the relative stereochemistry of the alkene moiety.[259] It is important to point out that these trends in *cis/trans* stereochemistry are opposite to the effects observed in unsaturated polyolefins (natural rubber and gutta-percha). These differences are non-intuitive and reconciling such observations is important to the advancement of the field. Switchable *cis/trans* photo-isomerisation has been used as a post-polymerisation technique to alter the stereochemical configuration of sulfur-rich acetylenic polymers. It was found that the optical application potential of the 100% *trans (Z)*-double bond-containing polymer was greater (*ca*. 3X) when compared to the analogous polymers with low *cis/trans* ratios, consequently demonstrating a dependence of opto-electronic properties on stereochemistry.[256] Several other studies have utilised the stereo-controlled thiol-yne polymerisation to synthesise new structures; however, the effect of stereochemistry on the properties of the polymers has to date not been investigated.[261-264] Similarly, other nucleophilic addition reactions (such as phenol-yne[263] or amino-yne)[265-269] have yielded stereo-controlled unsaturated polymers, but structure-property relationships were also not investigated, most likely on account of the initial difficulty to control the *cis*/*trans* ratio of the resultant polymers in these reactions. In many cases certain limitations, such as widely variable molecular weights between isomeric polymers and/or different overall material compositions, precluded direct material comparisons.

Other polymers with double bonds in the backbone

Polynorbornenes are a very important commodity polymer class. They are most commonly synthesised from ring opening metathesis polymerisation (ROMP) of norbornenes and the stereochemistry of the resultant C=C bond in the backbone can be tuned accordingly.[270-272] It is possible to synthesise stereo-pure polynorbornene[270-272] with judicious choice of catalyst and careful manipulation of the reaction conditions. For example, the use of Grubbs-type ruthenium based catalysts, particularly with bulkier monomers, results in predominantly *cis*-polynorbornene.[273] Employing Schrock-type molybdenum or tungsten catalysts can also yield stereo-controlled materials.[274,275] Additionally, tacticity must be considered in polynorbornenes (due to *endo/exo* isomerism) leading to four possible stereo-isomeric structures and it is synthetically possible to access all stereo-pure structures.[275] However, most reports (apart from a theoretical structure-property investigation)[276] have focussed exclusively on developing stereo-controlled synthetic methods with minimal investigation of stereochemical influence on material properties. Thus, there are significant opportunities to characterise the physical properties of stereopure polynorbornenes.

The extension of ROMP methodologies to create polyacetylene provides an interesting method by which to create materials with high *cis*-double bond contents, yet this methodology has not been fully explored in this respect. Instead, polyacetylene is more commonly accessed by coordination-insertion polymerisation methods. It is the simplest, yet arguably, the most fundamental polymer in the field of conducting polymers and by examining its properties another critical stereochemistry lesson can be demonstrated.[277] The geometry of polyacetylene can either be *cis* or *trans* and can be controlled through modification of the reaction conditions.[278] Apart from the observation that *cis*-polyacetylene[279] is rubbery and somewhat elastomeric[279] while *trans*-polyacetylene is much more brittle and crystalline, the *trans* isomer has greater conductivity by several orders of magnitude due to increased electron delocalisation along the backbone caused by improved orbital overlap.[278,280] Thus, opto-electronic properties are also highly sensitive to stereochemistry. Stilbene (1,2-diphenylethylene) is another simple moiety that appears suitable for incorporation into conjugated polymers since it possesses a photo-isomerisable C=C bond between the phenyl rings. However, it has not found widespread application in this area.[281] The stilbene moiety is notorious for a short lifetime of the *cis* isomer and overall photo-chemical instability (*e.g.* photo-crosslinking and production of oxidative side products).[282] Moreover, photo-oxidative issues can be exacerbated for extended conjugated systems. Poly(azomethine)s are an alternative system that contain -HC=N- moieties (isoelectronic to HC=CH groups present in archetypal conjugated polymers) and theoretically possess *cis/trans* isomerism. Importantly, these species avoid the photo-oxidative and chemical instability that hamper stilbenes since the imine bond is thermodynamically stabilised *via* conjugation.[283-287] A relatively recent aza-Wittig protocol was used to produce crystalline *trans*-poly(azomethine)s capable of supramolecular self-assembly.[288] However, the stereochemistry of the imine bond is rarely mentioned and only structures featuring the more stable *trans* isomer have been noted.[288,289] Thus, stereochemistry has not yet been fully explored and there are significant opportunities in this area if synthetic methods are developed to access polymers with high *cis* content. Furthermore, as a consequence of the robust nature of the conjugated imine functionality it could be harnessed as a phototunable π-bond.

Ring-based polymers

The introduction of aliphatic rings into polymer backbones can impart rigidity (*i.e.* improved thermal properties) and provide access to materials with fixed stereochemistry along the polymer backbone. The most common ring systems in such polymers are derived from 1,4-cyclohexylene which is of particular interest because it can be sustainably sourced and often incorporated into robust plastics.[290] 1,4-Cyclohexanedimethanol (CHDM) was copolymerised with 2,5-furandicarboxylate to yield materials with various *cis/trans* contents. The *trans* content (25–98%) of CHDM was positively correlated to the degree of crystallinity, T_g, T_m (maximum T_m of 252 °C for 98% *trans* content) and improved material toughness.[291] Similar trends have been found in polyamides containing 1,4-cyclohexanedicarboxylic acid (CHDA) or 1,4-diaminocyclohexane (DACH) where higher *trans* content correlated with improved thermal properties.[292] Investigations on the stereochemistry of other 1,4-cyclohexylene based aliphatic polyesters also found increased crystallinity and better thermal properties for high *trans* formulations.[293-297] However, a triblock copolymer system incorporating *cis*-1,4-cyclohexylene showed increased elongation at break and concomitantly decreased tensile modulus and strength, even though the crystallinity was reduced compared to the *trans* analogue.[298] However, it should be noted that this polymer possessed properties analogous to TPEs, *i.e.* hard-soft domains, which must be considered. Nevertheless, this result beckons one to be cautious about generalising stereochemistry-based structure property relationships. The significant literature

examining 1,4-cyclohexylene based polymers demonstrate stereochemical tuning of material properties and it is encouraging to see thorough structure-property relationships being developed in these systems.

Currently, polymers derived from sugar-based monomers are being intensely investigated since they are relatively inexpensive, exhibit stereochemical diversity, and the renewability of carbohydrates provides added advantage to petrochemical counterparts.[299] Carbohydrate monomers featuring the fused ring 1,4:3,6-dianhydrohexitols (or isohexides) have garnered much attention. Isohexides are particularly interesting since they possesses structural diversity according to the relative stereochemistry at the hydroxyl group on the fused ring.[300] The hydroxyl group lends itself to facile functionalisation providing access to a wide range of stereo-specific monomers. Additionally, the imparted rigidity from the fused ring unit and non-toxic nature of the isohexides can be incorporated into mechanically robust, biocompatible polymers.[301] Isosorbide (endo/exo –OH groups) and isomannide (endo/endo –OH groups) are both sourced from depolymerised polysaccharides[51] and commercially available, however isoidide (exo/exo –OH groups) is only synthesised on a small scale from isosorbide[302] or isomannide.[56,57303-305] In most cases, the hydroxyl group is transformed to a more reactive group (such as an amine, carboxylic acid, or isocyanate) that is amenable for step-growth polymerisation.[301] Amino-functionalised isohexides afforded a series of polyamides where the T_g (when observed before decomposition) was dependent on stereochemistry (T_g of isosorbide < isomannide < isoidide) and the isoidide polymers had the greatest degree of crystallinity.[306] Similar thermal trends were found in isohexide-containing polyacetals[307], polyesters,[308,309] and isohexide-based polyureas/polyurethanes[310] with observable differences in physical appearance noted on some occasions.[311] Polyurethanes incorporating lactone units (analogous to isohexides) displayed similar stereochemistry trends. The endo/endo version (D-mannaro dilactone) displayed superior thermal properties to the endo/exo (D-glucaro dilactone) polymer.[312] Polytriazoles, synthesised from isohexide-azides and isohexide-alkynes have also been investigated. Materials featuring isomannide displayed the best thermal properties and the T_g was markedly lowered by the introduction of isosorbide or isoidide units.[313,314] Isohexides have also been paired with other renewable monomers such as hydroxymethylfurfural in copolymer compositions. Surprisingly, the isosorbide derivatives possessed superior thermomechanical properties to the isomannide counterpart for similar molecular weights. However, rheological data suggested that the entanglement molecular weight (M_e) for the isosorbide structure was lower, which could explain the apparent discrepancy.[315] Observations on the copolymer systems highlights the difficulties associated with determining structure-property relationships for polymers with stochastic monomer sequences (*i.e.* random sequences of *endo-exo*, *endo-endo*, and *exo-exo* diads or copolymer compositions) since generic structure-property trends can break down. Thus, there remains considerable work to synthesise and fully characterise such complex copolymers. Despite the emergence of some stereochemical trends, again, the use of polycondensation reactions with A-A/B-B type isosorbide-based monomers can result in regiochemical differences between materials. These methods typically yield amorphous polymers (isomannide and isoidide yield more crystalline, regio-regular architectures) which is to be expected as a result of the reduced order of the system.[316,317] Again, this highlights that regiochemistry of the polymer structure cannot be ignored if present since it can distort structure-property relationships.

The implementation of sugar-based building blocks provides a facile platform to robust, stereo-defined materials since the stereo-pure monomers are easily sourced and derivatised. As such, a large number of recent studies report on sugar derived polymers using isohexides or isohexide derivatives with defined stereochemistry.[301,307,310,311,313,315,317-321] However, most have either failed to assess mechanical properties and/or overlooked the influence of stereochemistry in this regard.

Additionally, in some cases only certain derivatives (most commonly isosorbide) are synthesised and/or characterised because reactivity differences can emerge among isomers. The net effect is a resulting gap in the literature where a thorough analysis of stereochemistry-property relationships is missing. Moving forward, such analyses need to be considered more thoroughly if the true potential of stereochemistry on the resulting materials properties is to be more fundamentally understood. With a plethora of new materials being reported every year, this data could expedite the rational design of materials with targeted mechanical properties.

Stereocomplexation

Introduction to stereocomplexation

Each polymer chain usually possesses a vast quantity of possible conformations due to the sheer number of atoms and the rotation of atoms between chemical bonds. For any given material the inter- and intrachain interactions among unimers (van der Waals forces, dipole-dipole, H-bonding) largely govern the resultant properties. However, there is a large degree of disorder in most macromolecular systems. As such, efforts to increase the molecular order within materials are highly desirable. The mixing of two different polymers results in a material that may possess different properties of either singular component. If such a complex is composed of isomeric polymers that differ in terms of tacticity or chirality, then it can be referred to as a stereocomplex that generally features enhanced molecular order. As such, stereocomplexation has emerged as a powerful tool to improve the thermal and/or mechanical properties of materials. Although the first instance of stereocomplexation was demonstrated for polyelectrolytes,[322] the concept received considerably more attention after stereocomplexes of iPMMA with sPMMA were isolated (**Figure 5**).[323,324] Numerous classes of polymers have since been isolated as stereocomplexes and have been broadly covered in other reviews.[325,326] In this section, the main concepts of stereocomplexation and its primary effects on material properties are best illustrated by examining PMMA alongside other renewable polymers such as PLA or PHB.
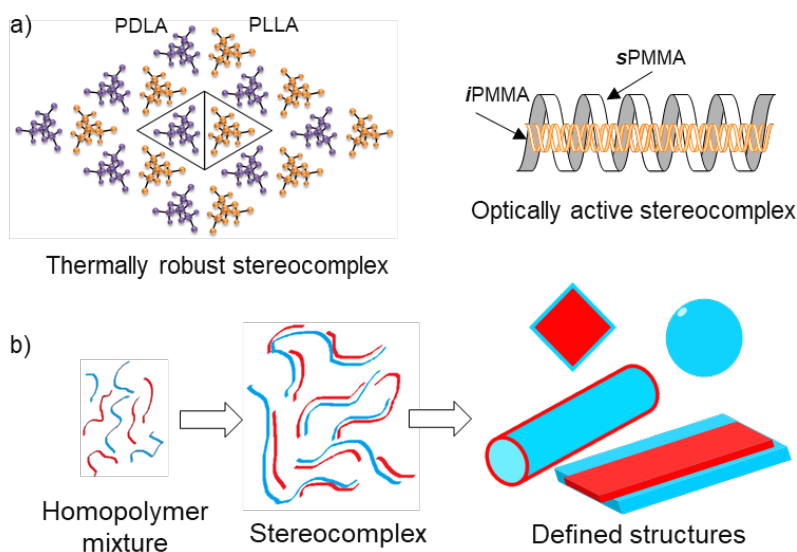

Figure 5. Stereocomplex formation (a) and their use to form higher order structures (b).

PMMA

Most principles of stereocomplexation were developed by studying PMMA where the aggregation behaviour was found to be a complex process showing a dependence on numerous factors including polymer stereopurity, stoichiometry, solvent and respective concentration, temperature/thermal history and local structure of aggregated sequences.[327,328] Often stereocomplexes are formed by mixing various ratios of stereopure homopolymers; however, it is also possible to induce tacticity and stereocomplexes during polymerisation. The polymerisation of MMA in the presence of iPMMA preferentially produces sPMMA chains and *vice versa* leading to the isolation of a stereocomplex (sc-PMMA).[329] Stereocomplexes can also be formed between distinct polymers *e.g.* blends of block copolymers with the stereopure unit acting as a sort of templating agent. Although PMMA may be regarded as elementary within polymer chemistry since it has been studied for decades, it continues to appear at the core of numerous innovative studies. PMMA stereocomplexes were formed within multi-block TPEs leading to a significant improvement of thermal properties relative to non-complexed analogues (**Figure 2**).[330-336] In such systems the stereocomplexed PMMA segments were implicated as physical cross-links. The *in situ* stereocomplexing polymerization of methyl methacrylate furnished sc-PMMA that was highly crystalline, but surprisingly optically transparent as well.[337] PMMA stereocomplexes have also been leveraged as reversible switches in network materials[338-340] or as templates for stereoselective polymerisation.[341] Of late, PMMA stereocomplexed structures have displayed utility in the development of higher order supramolecular assemblies.[189,190,218,219,221,342] More generally, since stereocomplexes are highly precise systems, well-defined cavities are also formed between the constituent polymer chains. Recently, optically active PMMA stereocomplexes were synthesised by placing iPMMA into the helical cavity of sPMMA *via* a helix-sense inclusion process (**Figure 5**).[190] A more impressive example involved the inclusion of C_{60} fullerene within a cross-linked methacrylate complex.[343] Interestingly, the inclusion complex exhibited a novel transition (T_m inclusion complex = 205 °C) that was not present in the fullerene, homopolymer, or the annealed blend.

PLA and other degradable polymers

Despite its attractiveness as a renewable polymer, industrially-produced PLLA is still a very brittle material due to its slow crystallisation rate and poor thermal stability.[344,345] PLA stereocomplexation, first discovered by Ikada *et al.* in 1987,[346] was shown to create materials with a higher heat resistance than PLLA. An equimolar blend of PLLA and PDLA produced a PLA stereocomplex (*sc*-PLA) that melted at approximately 230 °C, *ca.* 50 °C higher than the homochiral polymer. It has since been shown that stereocomplexation between PLLA and PDLA can occur in solution, in the solid (bulk) state from the melt, during polymerisation, or during hydrolytic degradation. Extensive studies have revealed that stereocomplexation is an intricate phenomenon which is governed by many parameters such as the PLLA/PDLA blend ratio,[347] molecular weight,[348,349] processing methodology,[350-352] and additives or nucleating agents.[353-355] All of these parameters ultimately influence the crystallisation efficiency of the *sc*-chains *versus* the homocrystallisation which can be a detrimental competing reaction. Beyond simple blends, non-blended stereoblock PLA (*sb*-PLA) also displays similar behaviour. In essence, stereocomplexation is possible as long as L-lactide (or L-lactyl) unit sequences and D-lactide (or D-lactyl) unit sequences coexist in a system.[356,357] The stereocomplex features the multisite hydrogen bonding interactions between L-lactyl and D-lactyl unit sequences and gives rise to a double-helical microstructure which possesses the enhanced thermal properties outlined. As may be expected, the more densely packed crystal structure and chain packing that originates from stronger hydrogen bonds between the enantiomeric PLA chains[358,359] results in a stereocomplexed structure that has different mechanical and rheological

properties compared to isotactic PLA or racemic structures.[360-362] Notably, *sc*-PLA displays increased tensile strength and Young's modulus, and reduced elongation at break compared to the homochiral materials.[347,363,364] The effect of structure is also evident from the slower hydrolytic biodegradation profile of the PLLA/PDLA blends compared to their homochiral analogues.[350,365] Finally, since PLA is inherently polymorphic the crystallinity of *sc*-PLA blends can be specifically adjusted by varying compositional ratios.[366] This is particularly attractive and gives a modular platform for a range of applications.

The copolymerisation of enantiopure lactides with a large battery of comonomers enables the synthesis of various architectures such as block, statistical, graft and star structures which are tailor-made for specific applications and still capable of stereocomplexation.[360,367,368] Undoubtedly, the principal application of PLA is as a synthetic, degradable biomaterial and stereocomplexation has played a leading role in the novel and 'smart' biomaterials that have distinctive and tunable features (*e.g.* hydrolytic degradation, self-assembly, physical stability and bioactivity). Moreover, stereocomplexation provides a new path to create diverse micro- and nano-structures (*e.g.* micelles) which are critically important for biomedical applications (**Figure 5**).[369,370] In order to improve water solubility PLA is commonly paired with hydrophilic polymers such as di- and tri-block PLA-PEG copolymer architectures.[371-377] When these block copolymers are placed in aqueous environments they form micelles that can be applied as drug delivery platforms. The overall stability of the micelles are strongly dependent upon the tacticity of PLA, with *sc*-PLA containing micelles exhibiting higher stability (lower critical micelle concentration) encapsulation efficiencies and more controlled drug release profiles.[372,373,378] In addition to PEG, polysaccharides such as Dextran have also been combined with *sc*-PLA to produce robust micelles for drug delivery.[379] Electrospun *sc*-PLA has also been investigated as a promising scaffold material.[380] Recent studies have demonstrated that stereocomplexed PLA nanofibers exhibit a much slower degradation profile and thus provoke a lower degree of inflammation *in vivo* than the homochiral PLLA or atactic P(*rac*-LA) nanofibers.[381-386] Furthermore, *sc*-PLA based hydrogels outperform non-stereocomplexed PLA counterparts in many metrics including hydrolytic stability, controlled release and toughness.[387-395] Furthermore, the stereocomplexation of PLA has been used to induce a morphology switch between cylindrical micelles of each homochiral PLA-*b*-PAA (poly(acrylic acid)) to create spherical micelles that contain stereocomplexed PLA in the core.[396] This discovery potentially points the way to using stereochemistry to determine function beyond just controlling molecular and macroscopic properties of polymers. The effect of PLA's stereochemistry on templated inorganic nanostructures has been investigated and shown to be a determining factor on the possible morphological control of block copolymers, providing supramolecular structures with a hierarchical order, as characterized by the distinctive vertical and horizontal growth of toroidal nanostructured inorganic features.[397] These robust nanostructures with thermal and mechanical stability are suitable for a low-dielectric insulating media and etching masks in microelectronics or for material encapsulation and macromolecular assemblies to transport and deliver biologically active agents. Recent advances in synthetic techniques in combination with the advantages PLA stereocomplexation provides have opened new pathways for designing new organic/inorganic polymer hybrids which would create entirely novel compositions with distinct properties.[367]

Secondary to biomedical applications, PLA has been intensely studied as a biodegradable alternative to vinyl plastics and more specifically as a hydrolytically degradable polyester. PLA has long been studied as a sustainable substitute for polystyrene leading to the utilisation of PLA as the 'hard' block in TPEs in which another renewable monomer, polymenthide (PM), is applied as the 'soft' block (**Figure 2**). The thermal and mechanical performance of reported PLA-based TPEs show a strong dependence on the stereoregularity of the PLA semi-crystalline block and the enhancement of the

physical interactions (physical crosslinking and stereocomplexation) between the hard segments.[398-402] In such TPEs, the Young's modulus and yield strength decrease in the order *sc*PLA < PLLA < poly(*rac*-LA) while a trend in ductility is less defined. Impressively, only incorporating 5% of the PDLA-*b*-PM-*b*-PDLA into 95% PLLA-*b*-PM-*b*-PLLA resulted in comparable mechanical properties to those of the 50:50 blend, which illustrates the effectiveness of stereocomplexation upon polymer properties.[401] These studies have provided a feasible approach to control the morphology and physical properties of ABA-type TPEs by manipulation of PLA stereoregularity and stereocomplexation. The renewable nature of these self-assembled materials should lead to sustainable high-performance plastics. PLA is currently the gold standard for implantable biomedical devices on account of its long history of successful use *in vivo*. More recently however it has also become the benchmark biosourced polyester, but its brittle nature and insufficient toughness has limited its competitiveness against more established materials. PLA stereocomplexation has opened up a new way to broaden the range of properties that are unattainable with homochiral or atactic PLA alone. Access to controlled polymerisation techniques has afforded an array of functional PLA-based copolymers with unique architectures and the stereocomplexation between the enantiomeric PLLA and PDLA segments has enabled access to many new materials' features such as novel chemical functionalities, bioactivities, as well as smart properties tailored for specific applications. Potential developments will likely come from *sc*PLA with complex topologies (*e.g.* cyclics, hyperbranched, grafts) leading to materials with unexpected properties. To this end, controlled micro- and nano-scale structures will continue to provide great opportunities in biomedicine. Additionally, other homostereocomplexes have been reported for a few renewable polymers such as poly(propylene succinate),[142] tartaric acid derived polyamides,[403-405] poly(propylene carbonate),[406] poly(limonene carbonate)[407,408] and an infinitely recyclable *trans*-cyclohexyl-ring-fused γ-butyrolactone polymer.[409,410] A particularly interesting example of alternative stereocomplexes are heterostereocomplexes which are materials formed between degradable polymers possessing different backbone architectures.[411] Heterostereocomplexes of PHBs and PLLA were recently investigated and such complexes feature enhanced thermal properties.[412-415] As it stands, there exists a massive library of potential heterostereocomplexes and other interesting materials will certainly be discovered. These developments in stereocomplexation are expected to place stereochemistry at the forefront of renewable polymer advancement.

Conclusion

Despite being studied for several decades, polymer stereochemistry is still a fledgling field. The sheer number of known (and potential) polymers and the inherent complexity of such large molecular structures can obfuscate stereochemistry effects and trends. Furthermore, access to stereochemically-defined structures is often difficult and novel polymerisation methods are still required to be actively developed. Establishing standard structure-property relationships that correlate stereochemistry to bulk properties remains challenging and it will likely never be fully realised in a truly universal manner between all polymers, but it could be greatly improved within individual polymer classes to enhance the rational design of future materials. In order to do so, the consideration of stereochemistry should become a more standard feature in polymer characterisation. We envision that many breakthrough advancements in materials development and nanotechnology will feature some sort of stereochemical enhancement since biopolymer function and performance is so intimately connected to the 3-dimensional arrangement of atoms. It will be necessary to raise the research profile of the importance of stereochemistry in determining material properties so that it is no longer overlooked and becomes a key question to be answered when evaluating polymers with distinct stereochemical configurations.

Clearly one of the main aspects that stereochemical definition in polymers elicits is a change in crystallinity within the material. While this has already been seen to affect the properties of thermoplastic elastomers, the control over this property could also see much broader application. Beyond the control of mechanical properties and hydrolytic degradation behaviour that is well known to be related to the degree of crystallinity, it could also lead to changes in barrier properties of films and water penetration which could ultimately enhance the applicability of the materials for food storage (amongst other applications). Indeed, if the chirality can be retained when swollen or in solution (as with the helical polymers), they may have rich applications as inexpensive chiral separation agents and in enantioselective catalysis supports. The ability to control crystallinity through stereochemical purity or stereocomplexation also leads to opportunities to control self-assembly processes through concepts like crystallisation-driven self-assembly to control particle morphology and dimensions or through control of higher order structures to control conductivity.[416-418 419-422]

While stereocomplexation can largely be applied to further strengthen materials through increased crystallinity, the complimentary and highly regular interactions between polymer chains also provides further opportunity to drive the field. This may be further leveraged to design materials that have controllable adhesion properties or through the use of stereochemistry to switch between self-assembled states. Stereocomplexation also enables the placement of different functional groups close to one another on solid materials but the ability of polymers like polymethacrylates to form inclusion complexes also presents different opportunities to exploit in host-guest interaction systems as well as bottom-up design of nanotechnology.

A promising emerging area in polymer stereochemistry is the incorporation of stereochemically dynamic, switchable moieties. Such moieties enable the switching between isomers that can readily or less readily crystallise and hence the properties of the bulk material can in theory be controlled by the application of an external stimulus (*e.g.* heat, light). Such a concept could potentially be extended to driving application such as actuators or through changes in conductivity and may be critical in shaping the soft robotics field. A recent study employed *cis* to *trans* photoisomerisation of poly(p-phenylenevinylene) block copolymers to induce CDSA to yield semiconducting nanofibers.[423] Photo-switchable azobenzene moieties have been used to reversibly alter thermal properties in linear structures[424,425] or mechanical properties in networks.[426-431] The same moiety was critical to the all-optical control of shape deformation and shape restoration in photoresponsive liquid crystal elastomers.[432] Furthermore, the dynamic nature of azobenzene moiety was employed to create light-driven chiroptical switches.[433,434] A chiral π-donor (*i.e.* electron rich) gelator self-assembled into a dynamic helix which after the addition of an achiral π-acceptor led to the material reassembling to include the π-acceptor in a composite helix thus transferring energy (circularly polarised light) and chirality to the achiral moiety.[435] Such a system is reminiscent of the soldier-sergeant mechanisms in helical polymer chirality but highlights the concept of dynamic systems and the potential to exchange information between molecules. It is possible that significant developments in this field may enable transfer of information (*e.g.* chirality)[436] between molecules.

Beyond these opportunities, the control over complex, readable sequences in polymers may be possible through stereochemically controlled polymerisation to create materials for data storage. This creation of materials that more closely mimic nature's polymers through controlling both aspects could, with the combination of sequence control with stereochemistry, also uniquely enable advances in synthetic biology or mechanisms by which to direct or control other biological processes. The scope to design polymers with specific stereochemistry and functional group placement has already provided many materials' advances. However, with further synthetic

advances and its application to new challenges there remains a significant scope for the stereochemical control of materials properties to impact a wide range of areas.

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Contributions

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