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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 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 ($T_m \sim 160^\circ\text{C}$) 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 Natta²¹ 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 1960⁵ 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, $T_m \sim 250$ °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 ($\Delta T_g > 70\text{ }^\circ\text{C}$).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 properties⁴³ 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 demand⁵⁴ 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, biocompatibility⁶⁰ 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 ($\bar{M}_n$), 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 $\sim 150\text{ }^\circ\text{C}$, 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 $\sim 180\text{ }^\circ\text{C}$ and a T_g near $50\text{ }^\circ\text{C}$. 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 $\sim 70\text{ MPa}$, 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.* $T_m \sim 180\text{ }^\circ\text{C}$ 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 ($\Delta T_m > 100\text{ }^\circ\text{C}$) 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 microstructures¹⁰⁰⁻¹⁰² that may yield promising new functional materials. Furthermore, there is interest in producing copolymers by combining PHB with other polyhydroxyalkanoates¹⁰³⁻¹¹⁰ 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 atactic¹³² 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 CO₂ 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 CO₂, 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 morphology¹⁶²⁻¹⁶⁶ 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 polyacetylene 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 counterion (D- or L-camphorsulfonic acid), have been utilised to create highly ordered conducting micro/nanofibers,¹⁷³⁻¹⁷⁶ nanosheets¹⁷⁷ 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 complexation¹⁷⁹ 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 information¹⁸⁴ 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

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(quinoline-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 Majority¹⁹³ 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 improved²⁰⁸⁻²¹¹ 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, polyisocyanates²¹⁵ and polysilanes²¹⁶ 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” superstructures²¹⁷ 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 *cPI*) and gutta-percha (*trans*-polyisoprene or *tPI*). 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 (*cPI* and *tPI* respectively) possess divergent properties that are dependent on main-chain stereochemistry. Examining the thermal properties, the T_g is similar between the isomers; however *tPI* 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. *cPI* is amorphous, soft, flexible and elastic whereas *tPI* 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 of 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 CH₂ 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 Ziegler-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 thermo-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 ($\Delta T_g = 20$ °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 = $1495 \pm 66\%$) while high *trans* materials (32% *cis*) were much softer (ultimate tensile strength = 2.8 ± 0.4 MPa and elongation at break = $2970 \pm 137\%$). 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-yne²⁶³ 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 polynorbornene²⁷⁰⁻²⁷² 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*-polyacetylene²⁷⁹ is rubbery and somewhat elastomeric²⁷⁹ 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 possess 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 polysaccharides⁵¹ and commercially available, however isoidide (exo/exo –OH groups) is only synthesised on a small scale from isosorbide³⁰² or isomannide.^{56,57,303-305} 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 polyacetals³⁰⁷, polyesters,^{308,309} and isohexide-based polyureas/polyurethanes³¹⁰ 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 materials³³⁸⁻³⁴⁰ 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 C₆₀ 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, polymethide (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⁻

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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.

Highlighted references

Coates, G. W. & Waymouth, R. M. Oscillating stereocontrol: A strategy for the synthesis of thermoplastic elastomeric polypropylene. *Science* **267**, 217 (1995).

Ishihara, N., Seimiya, T., Kuramoto, M. & Uoi, M. Crystalline syndiotactic polystyrene. *Macromolecules* **19**, 2464-2465, (1986).

Wang, J. *et al.* Modification of poly(ethylene 2,5-furandicarboxylate) (PEF) with 1, 4-cyclohexanedimethanol: Influence of stereochemistry of 1,4-cyclohexylene units. *Polymer* **137**, 173-185, (2018).

Wu, J. *et al.* Fully isohexide-based polyesters: synthesis, characterization, and structure–properties relations. *Macromolecules* **46**, 384-394, (2013).

Ban, H. T. *et al.* A new approach to styrenic thermoplastic elastomers: synthesis and characterization of crystalline styrene–butadiene–styrene triblock copolymers. *Macromolecules* **39**, 171-176, (2006).

Bell, C. A. *et al.* Independent control of elastomer properties through stereocontrolled synthesis. *Angew. Chem. Int. Ed.* **55**, 13076-13080, (2016).

W., J. C. K. *et al.* Metal-free alkyne polyhydrothiolation: synthesis of functional poly(vinylenesulfide)s with high stereoregularity by regioselective thiclick polymerization. *Adv. Funct. Mater.* **20**, 1319-1328, (2010).

Sun, L. *et al.* Structural reorganization of cylindrical nanoparticles triggered by polylactide stereocomplexation. *Nature Commun.* **5**, 5746, (2014).

Auriemma, F. *et al.* Stereocomplexed poly(limonene carbonate): A unique example of the cocrystallization of amorphous enantiomeric polymers. *Angew. Chem. Int. Ed.* **54**, 1215-1218, (2014).

Vidal, F., Falivene, L., Caporaso, L., Cavallo, L. & Chen, E. Y. X. Robust cross-linked stereocomplexes and C₆₀ inclusion complexes of vinyl-functionalized stereoregular polymers derived from chemo/stereoselective coordination polymerization. *J. Am. Chem. Soc.* **138**, 9533-9547, (2016).

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Contributions

All authors contributed to the writing of this manuscript. J.C.W., A.P.D. and M.L.B. edited the manuscript into its final form

References

- 1 Jenkins, A. D. Stereochemical definitions and notations relating to polymers. *Pure Appl. Chem.* **53**, 733-752, (1981).
- 2 Wulff, G. Main-chain chirality and optical activity in polymers consisting of C-C chains. *Angew. Chem. Int. Ed.* **28**, 21-37, (1989).
- 3 Schildknecht, C. E., Gross, S. T., Davidson, H. R., Lambert, J. M. & Zoss, A. O. Polyvinyl isobutyl ethers. *Ind. Eng. Chem.* **40**, 2104-2115, (1948).
- 4 Natta, G. *et al.* Crystalline high polymers of α -olefins. *J. Am. Chem. Soc.* **77**, 1708-1710, (1955).
- 5 Natta, G., Corradini, P. & Bassi, I. W. Crystal structure of isotactic polystyrene. *Il Nuovo Cimento (1955-1965)* **15**, 68-82, (1960).
- 6 Fox, T. G. *et al.* Crystalline polymers of methyl methacrylate. *J. Am. Chem. Soc.* **80**, 1768-1769, (1958).
- 7 Coates, G. W. & Domski, G. J. in *Organotransition Metal Chemistry - From Bonding to Catalysis* (ed John F. Hartwig) Ch. 22. Polymerization and oligomerization of olefins, 1047-1100 (University Science Books, 2010).
- 8 Tabbà, H. D., Hijji, Y. M. & Abu-Surrah, A. S. in *Polyolefin Compounds and Materials: Fundamentals and Industrial Applications* (eds Mariam Al-Ali AlMa'adeed & Igor Krupa) Ch. Olefin polymerization, 51-77 (Springer International Publishing, 2016).
- 9 Domski, G. J., Rose, J. M., Coates, G. W., Bolig, A. D. & Brookhart, M. Living alkene polymerization: New methods for the precision synthesis of polyolefins. *Prog. Polym. Sci.* **32**, 30-92, (2007).
- 10 Busico, V. & Cipullo, R. Microstructure of polypropylene. *Prog. Polym. Sci.* **26**, 443-533, (2001).
- 11 Coates, G. W. Precise control of polyolefin stereochemistry using single-site metal catalysts. *Chem. Rev.* **100**, 1223-1252, (2000).
- 12 Resconi, L., Cavallo, L., Fait, A. & Piemontesi, F. Selectivity in propene polymerization with metallocene catalysts. *Chem. Rev.* **100**, 1253-1346, (2000).
- 13 Brintzinger Hans, H., Fischer, D., Mülhaupt, R., Rieger, B. & Waymouth Robert, M. Stereospecific olefin polymerization with chiral metallocene catalysts. *Angew. Chem. Int. Ed.* **34**, 1143-1170, (1995).
- 14 Natta, G. Properties of isotactic, atactic, and stereoblock homopolymers, random and block copolymers of α -olefins. *J. Polym. Sci.* **34**, 531-549, (1959).
- 15 Giller, C. *et al.* Synthesis, characterization, and electrospinning of architecturally-discrete isotactic-atactic-isotactic triblock stereoblock polypropene elastomers. *Macromolecules* **44**, 471-482, (2011).
- 16 Harney, M. B., Zhang, Y. & Sita, L. R. Discrete, multiblock isotactic-atactic stereoblock polypropene microstructures of differing block architectures through programmable stereomodulated living Ziegler-Natta polymerization. *Angew. Chem. Int. Ed.* **45**, 2400-2404, (2006).
- 17 Madkour Tarek, M. & Mark James, E. Mesoscopic modeling of the polymerization, morphology, and crystallization of stereoblock and stereoregular polypropylenes. *J. Polym. Sci., Part B: Polym. Phys.* **40**, 840-853, (2002).
- 18 Coates, G. W. & Waymouth, R. M. Oscillating stereocontrol: A strategy for the synthesis of thermoplastic elastomeric polypropylene. *Science* **267**, 217, (1995).
- 19 Mallin, D. T., Rausch, M. D., Lin, Y. G., Dong, S. & Chien, J. C. W. rac-[Ethylidene(1- η -5-tetramethylcyclopentadienyl)(1- η -5-indenyl)]dichlorotitanium and its homopolymerization of propylene to crystalline-amorphous block thermoplastic elastomers. *J. Am. Chem. Soc.* **112**, 2030-2031, (1990).

- 20 Collette, J. W. *et al.* Elastomeric polypropylenes from alumina-supported tetraalkyl Group IVB catalysts. 1. Synthesis and properties of high molecular weight stereoblock homopolymers. *Macromolecules* **22**, 3851-3858, (1989).
- 21 Natta, G., Pasquon, I. & Zambelli, A. Stereospecific catalysts for the head-to-tail polymerization of propylene to a crystalline syndiotactic polymer. *J. Am. Chem. Soc.* **84**, 1488-1490, (1962).
- 22 Thomann, R., Wang, C., Kressler, J., Jüngling, S. & Mülhaupt, R. Morphology of syndiotactic polypropylene. *Polymer* **36**, 3795-3801, (1995).
- 23 Lovinger, A. J., Lotz, B., Davis, D. D. & Schumacher, M. Morphology and thermal properties of fully syndiotactic polypropylene. *Macromolecules* **27**, 6603-6611, (1994).
- 24 De Rosa, C. & Corradini, P. Crystal structure of syndiotactic polypropylene. *Macromolecules* **26**, 5711-5718, (1993).
- 25 Ahmad, N., Di Girolamo, R., Auriemma, F., De Rosa, C. & Grizzuti, N. Relations between stereoregularity and melt viscoelasticity of syndiotactic polypropylene. *Macromolecules* **46**, 7940-7946, (2013).
- 26 Takebe, T., Yamasaki, K., Funaki, K. & Malanga, M. in *Syndiotactic Polystyrene : Synthesis, Characterization, Processing, and Applications* (eds Jürgen Schellenberg & Margaret W. Cohen) Ch. Properties, processing, and applications of syndiotactic polystyrene, 267-394 (Wiley, 2009).
- 27 Ishihara, N., Seimiya, T., Kuramoto, M. & Uoi, M. Crystalline syndiotactic polystyrene. *Macromolecules* **19**, 2464-2465, (1986).
- 28 Woo, E. M., Sun, Y. S. & Yang, C. P. Polymorphism, thermal behavior, and crystal stability in syndiotactic polystyrene vs. its miscible blends. *Prog. Polym. Sci.* **26**, 945-983, (2001).
- 29 Wang, C., Lin, C.-C. & Tseng, L.-C. Miscibility, crystallization and morphologies of syndiotactic polystyrene blends with isotactic polystyrene and with atactic polystyrene. *Polymer* **47**, 390-402, (2006).
- 30 Cimmino, S., Pace, E. D., Martuscelli, E. & Silvestre, C. Syndiotactic polystyrene: crystallization and melting behaviour. *Polymer* **32**, 1080-1083, (1991).
- 31 Chen, K., Harris, K. & Vyazovkin, S. Tacticity as a factor contributing to the thermal stability of polystyrene. *Macromol. Chem. Phys.* **208**, 2525-2532, (2007).
- 32 Ishihara, N. Syntheses and properties of syndiotactic polystyrene. *Macromol. Symp.* **89**, 553-562, (1995).
- 33 Huang, C.-L., Chen, Y.-C., Hsiao, T.-J., Tsai, J.-C. & Wang, C. Effect of tacticity on viscoelastic properties of polystyrene. *Macromolecules* **44**, 6155-6161, (2011).
- 34 Annunziata, L. *et al.* On the crystallization behavior of syndiotactic-b-atactic polystyrene stereodiblock copolymers, atactic/syndiotactic polystyrene blends, and aPS/sPS blends modified with sPS-b-aPS. *Mater. Chem. Phys.* **141**, 891-902, (2013).
- 35 Annunziata, L., Sarazin, Y., Duc, M. & Carpentier, J. F. Well-defined syndiotactic polystyrene-b-atactic polystyrene stereoblock polymers. *Macromol. Rapid Commun.* **32**, 751-757, (2011).
- 36 Banerjee, S., Paira Tapas, K. & Mandal Tarun, K. Control of molecular weight and tacticity in stereospecific living cationic polymerization of α -methylstyrene at 0 °C using FeCl₃-based initiators: Effect of tacticity on thermal properties. *Macromol. Chem. Phys.* **214**, 1332-1344, (2013).
- 37 Chen, E. Y. X. Coordination polymerization of polar vinyl monomers by single-site metal catalysts. *Chem. Rev.* **109**, 5157-5214, (2009).
- 38 Ute, K., Miyatake, N. & Hatada, K. Glass transition temperature and melting temperature of uniform isotactic and syndiotactic poly(methyl methacrylate)s from 13mer to 50mer. *Polymer* **36**, 1415-1419, (1995).
- 39 Biroš, J., Larina, T., Trekoval, J. & Pouchlý, J. Dependence of the glass transition temperature of poly (methyl methacrylates) on their tacticity. *Colloid Polym. Sci.* **260**, 27-30, (1982).

- 40 Bywater, S. & Toporowski, P. M. Effect of stereostructure on glass transition temperatures of poly(methyl methacrylate). *Polymer* **13**, 94-96, (1972).
- 41 Katime, I. & Calleja Ricardo, D. Dynamic mechanical properties of isotactic PMMA. *Polym. Int.* **35**, 281-285, (1994).
- 42 Gillham, J. K., Stadnicki, S. J. & Hazony, Y. Low-frequency thermomechanical spectrometry of polymeric materials: Tactic poly(methyl methacrylates). *J. Appl. Polym. Sci.* **21**, 401-424, (1977).
- 43 Min, K. E. & Paul, D. R. Effect of tacticity on permeation properties of poly(methyl methacrylate). *J. Polym. Sci., Part B: Polym. Phys.* **26**, 1021-1033, (2003).
- 44 Semen, J. & Lando, J. B. The acid hydrolysis of isotactic and syndiotactic poly(methyl methacrylate). *Macromolecules* **2**, 570-575, (1969).
- 45 Loecker, W. D. & Smets, G. Hydrolysis of methacrylic acid–methyl methacrylate copolymers. *J. Polym. Sci.* **40**, 203-216, (1959).
- 46 Samal, S. & Thompson, B. C. Converging the hole mobility of poly(2-N-carbazoyl ethyl acrylate) with conjugated polymers by tuning isotacticity. *ACS Macro Lett.* **7**, 1161-1167, (2018).
- 47 Teator, A. J. & Leibfarth, F. A. Catalyst-controlled stereoselective cationic polymerization of vinyl ethers. *Science* **363**, 1439, (2019).
- 48 Severn, J. R. & Chadwick, J. C. *Tailor-made polymers*. (Wiley-VCH Verlag GmbH & Co. KGaA, 2008).
- 49 Chen, X., Caporaso, L., Cavallo, L. & Chen, E. Y. X. Stereoselectivity in metallocene-catalyzed coordination polymerization of renewable methylene butyrolactones: From stereo-random to stereo-perfect polymers. *J. Am. Chem. Soc.* **134**, 7278-7281, (2012).
- 50 Schneiderman, D. K. & Hillmyer, M. A. 50th Anniversary perspective: There Is a great future in sustainable polymers. *Macromolecules* **50**, 3733-3749, (2017).
- 51 Zhu, Y., Romain, C. & Williams, C. K. Sustainable polymers from renewable resources. *Nature* **540**, 354-362, (2016).
- 52 Gandini, A. & Lacerda, T. M. From monomers to polymers from renewable resources: Recent advances. *Prog. Polym. Sci.* **48**, 1-39, (2015).
- 53 Ragauskas, A. J. *et al.* The path forward for biofuels and biomaterials. *Science* **311**, 484-489, (2006).
- 54 Dudley, B. BP statistical review of world energy June 2017 (2017).
- 55 Lebreton, L. *et al.* Evidence that the Great Pacific Garbage Patch is rapidly accumulating plastic. *Sci. Rep.* **8**, 4666, (2018).
- 56 Cózar, A. *et al.* Plastic debris in the open ocean. *Proc. Natl. Acad. Sci. U. S. A.* **111**, 10239-10244, (2014).
- 57 Farah, S., Anderson, D. G. & Langer, R. Physical and mechanical properties of PLA, and their functions in widespread applications — A comprehensive review. *Adv. Drug Delivery Rev.* **107**, 367-392, (2016).
- 58 Södergård, A. & Stolt, M. Properties of lactic acid based polymers and their correlation with composition. *Prog. Polym. Sci.* **27**, 1123-1163, (2002).
- 59 Drumright, R. E., Gruber, P. R. & Henton, D. E. Polylactic acid technology. *Adv. Mater.* **12**, 1841-1846, (2000).
- 60 Albertsson, A. C. & Varma, I. K. Recent developments in ring opening polymerization of lactones for biomedical applications. *Biomacromolecules* **4**, 1466-1486, (2003).
- 61 Ikada, Y. & Tsuji, H. Biodegradable polyesters for medical and ecological applications. *Macromol. Rapid Commun.* **21**, 117-132, (2000).
- 62 Dechy-Cabaret, O., Martin-Vaca, B. & Bourissou, D. Controlled ring-opening polymerization of lactide and glycolide. *Chem. Rev.* **104**, 6147-6176, (2004).
- 63 Gross, R. A. & Kalra, B. Biodegradable polymers for the environment. *Science* **297**, 803-807, (2002).

- 64 Dove, A. P. Controlled ring-opening polymerisation of cyclic esters: polymer blocks in self-assembled nanostructures. *Chem. Commun.*, 6446-6470, (2008).
- 65 Stanford, M. J. & Dove, A. P. Stereocontrolled ring-opening polymerisation of lactide. *Chem. Soc. Rev.* **39**, 486-494, (2010).
- 66 Thomas, C. M. Stereocontrolled ring-opening polymerization of cyclic esters: synthesis of new polyester microstructures. *Chem. Soc. Rev.* **39**, 165-173, (2010).
- 67 Hong, M. & Chen, E. Y. X. Chemically recyclable polymers: a circular economy approach to sustainability. *Green Chem.* **19**, 3692-3706, (2017).
- 68 Chile, L.-E., Mehrkhodavandi, P. & Hatzikiriakos, S. G. A comparison of the rheological and mechanical properties of isotactic, syndiotactic, and heterotactic poly(lactide). *Macromolecules* **49**, 909-919, (2016).
- 69 Othman, N., Acosta-Ramírez, A., Mehrkhodavandi, P., Dorgan, J. R. & Hatzikiriakos, S. G. Solution and melt viscoelastic properties of controlled microstructure poly(lactide). *J. Rheol.* **55**, 987-1005, (2011).
- 70 Södergård, A. & Stolt, M. in *Poly(Lactic Acid)* Ch. 3. Industrial production of high molecular weight poly(lactic acid), 27-41 (Wiley, 2010).
- 71 Saeidlou, S., Huneault, M. A., Li, H. & Park, C. B. Poly(lactic acid) crystallization. *Prog. Polym. Sci.* **37**, 1657-1677, (2012).
- 72 Feng, L. *et al.* Thermal properties of polylactides with different stereoisomers of lactides used as comonomers. *Macromolecules* **50**, 6064-6073, (2017).
- 73 Inkinen, S., Hakkarainen, M., Albertsson, A.-C. & Södergård, A. From lactic acid to poly(lactic acid) (PLA): Characterization and analysis of PLA and its precursors. *Biomacromolecules* **12**, 523-532, (2011).
- 74 Garlotta, D. A literature review of poly(lactic acid). *J. Polym. Environ.* **9**, 63-84, (2001).
- 75 He, X. *et al.* Complex and hierarchical 2D assemblies via crystallization-driven self-assembly of poly(l-lactide) homopolymers with charged termini. *J. Am. Chem. Soc.* **139**, 9221-9228, (2017).
- 76 Sun, L. *et al.* Core functionalization of semi-crystalline polymeric cylindrical nanoparticles using photo-initiated thiol-ene radical reactions. *Polym. Chem.* **7**, 2337-2341, (2016).
- 77 Pitto-Barry, A., Kirby, N., Dove, A. P. & O'Reilly, R. K. Expanding the scope of the crystallization-driven self-assembly of polylactide-containing polymers. *Polym. Chem.* **5**, 1427-1436, (2014).
- 78 Sun, L. *et al.* Tuning the size of cylindrical micelles from poly(l-lactide)-b-poly(acrylic acid) diblock copolymers based on crystallization-driven self-assembly. *Macromolecules* **46**, 9074-9082, (2013).
- 79 Petzetakis, N., Walker, D., Dove, A. P. & O'Reilly, R. K. Crystallization-driven sphere-to-rod transition of poly(lactide)-b-poly(acrylic acid) diblock copolymers: mechanism and kinetics. *Soft Matter* **8**, 7408-7414, (2012).
- 80 Petzetakis, N., Dove, A. P. & O'Reilly, R. K. Cylindrical micelles from the living crystallization-driven self-assembly of poly(lactide)-containing block copolymers. *Chem. Sci.* **2**, 955-960, (2011).
- 81 Sharma, M. & Dhingra, H. K. Poly- β -hydroxybutyrate: A biodegradable polyester, biosynthesis and biodegradation. *BMRJ* **14**, 1-11, (2016).
- 82 Sudesh, K., Abe, H. & Doi, Y. Synthesis, structure and properties of polyhydroxyalkanoates: biological polyesters. *Prog. Polym. Sci.* **25**, 1503-1555, (2000).
- 83 Lee Sang, Y. Bacterial polyhydroxyalkanoates. *Biotechnol. Bioeng.* **49**, 1-14, (1996).
- 84 Yokouchi, M., Chatani, Y., Tadokoro, H., Teranishi, K. & Tani, H. Structural studies of polyesters: 5. Molecular and crystal structures of optically active and racemic poly (β -hydroxybutyrate). *Polymer* **14**, 267-272, (1973).
- 85 Cornibert, J. & Marchessault, R. H. Physical properties of poly- β -hydroxybutyrate: IV. Conformational analysis and crystalline structure. *J. Mol. Biol.* **71**, 735-756, (1972).

- 86 Alper, R., Lundgren, D. G., Marchessault, R. H. & Cote, W. A. Properties of poly- β -hydroxybutyrate. I. General considerations concerning the naturally occurring polymer. *Biopolymers* **1**, 545-556, (1963).
- 87 Tang, X. & Chen, E. Y. X. Chemical synthesis of perfectly isotactic and high melting bacterial poly(3-hydroxybutyrate) from bio-sourced racemic cyclic diolide. *Nature Commun.* **9**, 2345, (2018).
- 88 Bloembergen, S., Holden, D. A., Bluhm, T. L., Hamer, G. K. & Marchessault, R. H. Stereoregularity in synthetic β -hydroxybutyrate and β -hydroxyvalerate homopolymers. *Macromolecules* **22**, 1656-1663, (1989).
- 89 Bloembergen, S., Holden, D. A., Bluhm, T. L., Hamer, G. K. & Marchessault, R. H. Synthesis of crystalline β -hydroxybutyrate/ β -hydroxyvalerate copolyesters by coordination polymerization of β -lactones. *Macromolecules* **20**, 3086-3089, (1987).
- 90 Pearce, R. & Marchessault, R. H. Multiple melting in blends of isotactic and atactic poly(β -hydroxybutyrate). *Polymer* **35**, 3990-3997, (1994).
- 91 Pearce, R., Jesudason, J., Orts, W., Marchessault, R. H. & Bloembergen, S. Blends of bacterial and synthetic poly(β -hydroxybutyrate): effect of tacticity on melting behaviour. *Polymer* **33**, 4647-4649, (1992).
- 92 Kunze, C. *et al.* In vitro and in vivo studies on blends of isotactic and atactic poly (3-hydroxybutyrate) for development of a dura substitute material. *Biomaterials* **27**, 192-201, (2006).
- 93 Ligny, R., Hänninen Mikko, M., Guillaume Sophie, M. & Carpentier, J. F. Highly syndiotactic or isotactic polyhydroxyalkanoates by ligand-controlled yttrium-catalyzed stereoselective ring-opening polymerization of functional racemic β -lactones. *Angew. Chem. Int. Ed.* **56**, 10388-10393, (2017).
- 94 Ajellal, N. *et al.* Syndiotactic-enriched poly(3-hydroxybutyrate)s via stereoselective ring-opening polymerization of racemic β -butyrolactone with discrete yttrium catalysts. *Macromolecules* **42**, 987-993, (2009).
- 95 Amgoune, A., Thomas Christophe, M., Ilinca, S., Roisnel, T. & Carpentier, J. F. Highly active, productive, and syndiospecific yttrium initiators for the polymerization of racemic β -butyrolactone. *Angew. Chem. Int. Ed.* **45**, 2782-2784, (2006).
- 96 Rieth, L. R., Moore, D. R., Lobkovsky, E. B. & Coates, G. W. Single-Site β -diiminate zinc catalysts for the ring-opening polymerization of β -butyrolactone and β -valerolactone to poly(3-hydroxyalkanoates). *J. Am. Chem. Soc.* **124**, 15239-15248, (2002).
- 97 Kricheldorf, H. R. & Lee, S.-R. Polylactones. 35. macrocyclic and stereoselective polymerization of β -D,L-butyrolactone with cyclic dibutyltin initiators. *Macromolecules* **28**, 6718-6725, (1995).
- 98 Hocking, P. J. & Marchessault, R. H. Syndiotactic poly[(R,S)- β -hydroxybutyrate] isolated from methylaluminoxane-catalyzed polymerization. *Polym. Bull. (Berlin)* **30**, 163-170, (1993).
- 99 Abe, H., Matsubara, I., Doi, Y., Hori, Y. & Yamaguchi, A. Physical properties and enzymic degradability of poly(3-hydroxybutyrate) stereoisomers with different stereoregularities. *Macromolecules* **27**, 6018-6025, (1994).
- 100 Jaffredo Cédric, G., Chapurina, Y., Guillaume Sophie, M. & Carpentier, J. F. From syndiotactic homopolymers to chemically tunable alternating copolymers: Highly active yttrium complexes for stereoselective ring-opening polymerization of β -Malolactonates. *Angew. Chem. Int. Ed.* **53**, 2687-2691, (2014).
- 101 Carpentier, J. F. Discrete metal catalysts for stereoselective ring-opening polymerization of chiral racemic β -lactones. *Macromol. Rapid Commun.* **31**, 1696-1705, (2010).
- 102 Ajellal, N., Thomas Christophe, M. & Carpentier, J. F. Functional syndiotactic poly(β -hydroxyalkanoate)s via stereoselective ring-opening copolymerization of rac- β -butyrolactone and rac-allyl- β -butyrolactone. *J. Polym. Sci., Part A: Polym. Chem.* **47**, 3177-3189, (2009).

- 103 Xu, Y.-C., Ren, W.-M., Zhou, H., Gu, G.-G. & Lu, X.-B. Functionalized polyesters with tunable degradability prepared by controlled ring-opening (co)polymerization of lactones. *Macromolecules* **50**, 3131-3142, (2017).
- 104 Fagerland, J., Finne-Wistrand, A. & Pappalardo, D. Modulating the thermal properties of poly(hydroxybutyrate) by the copolymerization of rac- β -butyrolactone with lactide. *New J. Chem.* **40**, 7671-7679, (2016).
- 105 Barouti, G., Jarnouen, K., Cammas-Marion, S., Loyer, P. & Guillaume, S. M. Polyhydroxyalkanoate-based amphiphilic diblock copolymers as original biocompatible nanovectors. *Polym. Chem.* **6**, 5414-5429, (2015).
- 106 Jaffredo, C. G. & Guillaume, S. M. Benzyl β -malolactonate polymers: a long story with recent advances. *Polym. Chem.* **5**, 4168-4194, (2014).
- 107 Jaffredo, C. G., Carpentier, J.-F. & Guillaume, S. M. Organocatalyzed controlled ROP of β -lactones towards poly(hydroxyalkanoate)s: from β -butyrolactone to benzyl β -malolactone polymers. *Polym. Chem.* **4**, 3837-3850, (2013).
- 108 Jaffredo, C. G., Carpentier, J.-F. & Guillaume, S. M. Poly(hydroxyalkanoate) block or random copolymers of β -butyrolactone and benzyl β -malolactone: A matter of catalytic tuning. *Macromolecules* **46**, 6765-6776, (2013).
- 109 Ajellal, N., Thomas, C. M., Aubry, T., Grohens, Y. & Carpentier, J.-F. Encapsulation and controlled release of l-leuprolide from poly(β -hydroxyalkanoate)s: impact of microstructure and chemical functionalities. *New J. Chem.* **35**, 876-880, (2011).
- 110 Benvenuti, M. & Lenz Robert, W. Polymerization and copolymerization of β -butyrolactone and benzyl- β -malolactonate by aluminoxane catalysts. *J. Polym. Sci., Part A: Polym. Chem.* **29**, 793-805, (1991).
- 111 Yu, I., Ebrahimi, T., Hatzikiriakos, S. G. & Mehrkhodavandi, P. Star-shaped PHB-PLA block copolymers: immortal polymerization with dinuclear indium catalysts. *Dalton Trans.* **44**, 14248-14254, (2015).
- 112 MacDonald, J. P. *et al.* Tuning thermal properties and microphase separation in aliphatic polyester ABA copolymers. *Polym. Chem.* **6**, 1445-1453, (2015).
- 113 Aluthge, D. C. *et al.* PLA-PHB-PLA triblock copolymers: Synthesis by sequential addition and investigation of mechanical and rheological properties. *Macromolecules* **46**, 3965-3974, (2013).
- 114 Cross Edward, D., Allan Laura, E. N., Decken, A. & Shaver Michael, P. Aluminum salen and salan complexes in the ring-opening polymerization of cyclic esters: Controlled immortal and copolymerization of rac- β -butyrolactone and rac-lactide. *J. Polym. Sci., Part A: Polym. Chem.* **51**, 1137-1146, (2012).
- 115 Jeffery, B. J. *et al.* Group 4 initiators for the stereoselective ROP of rac- β -butyrolactone and its copolymerization with rac-lactide. *Chem. Commun.* **47**, 12328-12330, (2011).
- 116 Hiki, S., Miyamoto, M. & Kimura, Y. Synthesis and characterization of hydroxy-terminated [RS]-poly(3-hydroxybutyrate) and its utilization to block copolymerization with l-lactide to obtain a biodegradable thermoplastic elastomer. *Polymer* **41**, 7369-7379, (2000).
- 117 Barouti, G., Jaffredo, C. G. & Guillaume, S. M. Advances in drug delivery systems based on synthetic poly(hydroxybutyrate) (co)polymers. *Prog. Polym. Sci.* **73**, 1-31, (2017).
- 118 Paul, S. *et al.* Ring-opening copolymerization (ROCOP): synthesis and properties of polyesters and polycarbonates. *Chem. Commun.* **51**, 6459-6479, (2015).
- 119 Klein, R. & Wurm Frederik, R. Aliphatic polyethers: Classical polymers for the 21st century. *Macromol. Rapid Commun.* **36**, 1147-1165, (2015).
- 120 Childers, M. I., Longo, J. M., Van Zee, N. J., LaPointe, A. M. & Coates, G. W. Stereoselective epoxide polymerization and copolymerization. *Chem. Rev.* **114**, 8129-8152, (2014).
- 121 Kielland, N., Whiteoak Christopher, J. & Kleij Arjan, W. Stereoselective synthesis with carbon dioxide. *Adv. Synth. Catal.* **355**, 2115-2138, (2013).

- 122 Lu, X.-B., Ren, W.-M. & Wu, G.-P. CO₂ copolymers from epoxides: Catalyst activity, product selectivity, and stereochemistry control. *Acc. Chem. Res.* **45**, 1721-1735, (2012).
- 123 Ajiro, H., Widger, P. C. B., Ahmed, S. M., Allen, S. D. & Coates, G. W. in *Polymer Science: A Comprehensive Reference* (ed Martin Möller) Ch. Stereoselective ring-opening polymerization of epoxides, 165-181 (Elsevier, 2012).
- 124 Vaccarello, D. N. *et al.* Synthesis of semicrystalline polyolefin materials: Precision methyl branching via stereoretentive chain walking. *J. Am. Chem. Soc.* **140**, 6208-6211, (2018).
- 125 Childers, M. I. *et al.* Isospecific, chain shuttling polymerization of propylene oxide using a bimetallic chromium catalyst: A new route to semicrystalline polyols. *J. Am. Chem. Soc.* **139**, 11048-11054, (2017).
- 126 Ghosh, S., Lund, H., Jiao, H. & Mejía, E. Rediscovering the isospecific ring-opening polymerization of racemic propylene oxide with dibutylmagnesium. *Macromolecules* **50**, 1245-1250, (2017).
- 127 Widger, P. C. B. *et al.* Isospecific polymerization of racemic epoxides: a catalyst system for the synthesis of highly isotactic polyethers. *Chem. Commun.* **46**, 2935-2937, (2010).
- 128 Thomas, R. M. *et al.* Enantioselective epoxide polymerization using a bimetallic cobalt catalyst. *J. Am. Chem. Soc.* **132**, 16520-16525, (2010).
- 129 Hirahata, W., Thomas, R. M., Lobkovsky, E. B. & Coates, G. W. Enantioselective polymerization of epoxides: A highly active and selective catalyst for the preparation of stereoregular polyethers and enantiopure epoxides. *J. Am. Chem. Soc.* **130**, 17658-17659, (2008).
- 130 Peretti, K. L., Ajiro, H., Cohen, C. T., Lobkovsky, E. B. & Coates, G. W. A highly active, isospecific cobalt catalyst for propylene oxide polymerization. *J. Am. Chem. Soc.* **127**, 11566-11567, (2005).
- 131 Wu, B., Harlan, C. J., Lenz, R. W. & Barron, A. R. Stereoregular polymerization of (R,S)-propylene oxide by an alumoxane–propylene oxide complex. *Macromolecules* **30**, 316-318, (1997).
- 132 Lal, J. & Trick, G. S. Glass transformation temperatures of polymers of olefin oxides and olefin sulfides. *J. Polym. Sci., Part A: Polym. Chem.* **8**, 2339-2350, (1970).
- 133 Cesari, M., Perego, G. & Marconi, W. The crystal structure of isotactic poly (propylene oxide). *Die Makromolekulare Chemie* **94**, 194-204, (1966).
- 134 Stanley, E. & Litt, M. Crystal structure of d,l-poly(propylene oxide). *J. Polym. Sci.* **43**, 453-458, (1960).
- 135 McGrath, A. J. *et al.* Synthetic strategy for preparing chiral double-semicrystalline polyether block copolymers. *Polym. Chem.* **6**, 1465-1473, (2015).
- 136 Zhang, X.-H., Wei, R.-J., Zhang, Y. Y., Du, B.-Y. & Fan, Z.-Q. Carbon dioxide/epoxide copolymerization via a nanosized zinc–cobalt(III) double metal cyanide complex: Substituent effects of epoxides on polycarbonate selectivity, regioselectivity and glass transition temperatures. *Macromolecules* **48**, 536-544, (2015).
- 137 Li, B., Zhang, R. & Lu, X.-B. Stereochemistry control of the alternating copolymerization of CO₂ and propylene oxide catalyzed by SalenCrX complexes. *Macromolecules* **40**, 2303-2307, (2007).
- 138 Lu, X.-B. *et al.* Design of highly active binary catalyst systems for CO₂/epoxide copolymerization: Polymer selectivity, enantioselectivity, and stereochemistry control. *J. Am. Chem. Soc.* **128**, 1664-1674, (2006).
- 139 Cohen, C. T., Chu, T. & Coates, G. W. Cobalt catalysts for the alternating copolymerization of propylene oxide and carbon dioxide: Combining high activity and selectivity. *J. Am. Chem. Soc.* **127**, 10869-10878, (2005).
- 140 Lu, X. B. & Wang, Y. Highly active, binary catalyst systems for the alternating copolymerization of CO₂ and epoxides under mild conditions. *Angew. Chem. Int. Ed.* **43**, 3574-3577, (2004).

- 141 Qin, Z., Thomas Christophe, M., Lee, S. & Coates Geoffrey, W. Cobalt-based complexes for the copolymerization of propylene oxide and CO₂: Active and selective catalysts for polycarbonate synthesis. *Angew. Chem. Int. Ed.* **42**, 5484-5487, (2003).
- 142 Longo, J. M., DiCiccio, A. M. & Coates, G. W. Poly(propylene succinate): A new polymer stereocomplex. *J. Am. Chem. Soc.* **136**, 15897-15900, (2014).
- 143 Ellis, W. C. *et al.* Copolymerization of CO₂ and meso epoxides using enantioselective β -diiminate catalysts: a route to highly isotactic polycarbonates. *Chem. Sci.* **5**, 4004-4011, (2014).
- 144 Hua, Y. Z. *et al.* Highly enantioselective catalytic system for asymmetric copolymerization of carbon dioxide and cyclohexene oxide. *Chem. Eur. J.* **20**, 12394-12398, (2014).
- 145 Liu, Y., Ren, W. M., Liu, J. & Lu, X. B. Asymmetric copolymerization of CO₂ with meso-epoxides mediated by dinuclear cobalt(III) complexes: unprecedented enantioselectivity and activity. *Angew. Chem. Int. Ed.* **52**, 11594-11598, (2013).
- 146 Wu, G.-P. *et al.* Enhanced asymmetric induction for the copolymerization of CO₂ and cyclohexene oxide with unsymmetric enantiopure salen Co(III) complexes: synthesis of crystalline CO₂-based polycarbonate. *J. Am. Chem. Soc.* **134**, 5682-5688, (2012).
- 147 Ren, W.-M. *et al.* Highly active, bifunctional Co(III)-salen catalyst for alternating copolymerization of CO₂ with cyclohexene oxide and terpolymerization with aliphatic epoxides. *Macromolecules* **43**, 1396-1402, (2010).
- 148 Nakano, K., Nakamura, M. & Nozaki, K. Alternating copolymerization of cyclohexene oxide with carbon dioxide catalyzed by (salalen)CrCl complexes. *Macromolecules* **42**, 6972-6980, (2009).
- 149 Shi, L. *et al.* Asymmetric alternating copolymerization and terpolymerization of epoxides with carbon dioxide at mild conditions. *Macromolecules* **39**, 5679-5685, (2006).
- 150 Xiao, Y., Wang, Z. & Ding, K. Copolymerization of cyclohexene oxide with CO₂ by using intramolecular dinuclear zinc catalysts. *Chem. Eur. J.* **11**, 3668-3678, (2005).
- 151 Nakano, K., Nozaki, K. & Hiyama, T. Asymmetric alternating copolymerization of cyclohexene oxide and CO₂ with dimeric zinc complexes. *J. Am. Chem. Soc.* **125**, 5501-5510, (2003).
- 152 Cheng, M., Darling, N. A., Lobkovsky, E. B. & Coates, G. W. Enantiomerically-enriched organic reagents polymer synthesis: enantioselective copolymerization of cycloalkene oxides and CO using homogeneous, zinc-based catalysts. *Chem. Commun.*, 2007-2008, (2000).
- 153 Nozaki, K., Nakano, K. & Hiyama, T. Optically active polycarbonates: asymmetric alternating copolymerization of cyclohexene oxide and carbon dioxide. *J. Am. Chem. Soc.* **121**, 11008-11009, (1999).
- 154 Cohen, C. T., Thomas, C. M., Peretti, K. L., Lobkovsky, E. B. & Coates, G. W. Copolymerization of cyclohexene oxide and carbon dioxide using (salen)Co(III) complexes: synthesis and characterization of syndiotactic poly(cyclohexene carbonate). *Dalton Trans.*, 237-249, (2006).
- 155 Ciardelli, F., Benedetti, E. & Pieroni, O. Polymerization of racemic and optically active 4-methyl-1-hexyne. *Die Makromolekulare Chemie* **103**, 1-18, (1967).
- 156 Pu, L. The study of chiral conjugated polymers. *Acta Polym.* **48**, 116-141, (2003).
- 157 Inal, S., Rivnay, J., Suiiu, A.-O., Malliaras, G. G. & McCulloch, I. Conjugated polymers in bioelectronics. *Acc. Chem. Res.* **51**, 1368-1376, (2018).
- 158 Balint, R., Cassidy, N. J. & Cartmell, S. H. Conductive polymers: Towards a smart biomaterial for tissue engineering. *Acta Biomater.* **10**, 2341-2353, (2014).
- 159 Ibanez, J. G. *et al.* Conducting polymers in the fields of energy, environmental remediation, and chemical-chiral sensors. *Chem. Rev.* **118**, 4731-4816, (2018).
- 160 Kane-Maguire, L. A. P. & Wallace, G. G. Chiral conducting polymers. *Chem. Soc. Rev.* **39**, 2545-2576, (2010).
- 161 Torsi, L. *et al.* A sensitivity-enhanced field-effect chiral sensor. *Nat. Mater.* **7**, 412, (2008).

- 162 Yao, Y., Dong, H. & Hu, W. Ordering of conjugated polymer molecules: Recent advances and perspectives. *Polym. Chem.* **4**, 5197-5205, (2013).
- 163 Li, G., Zhu, R. & Yang, Y. Polymer solar cells. *Nat. Photonics* **6**, 153, (2012).
- 164 Tessler, N., Preezant, Y., Rappaport, N. & Roichman, Y. Charge transport in disordered organic materials and its relevance to thin-film devices: A tutorial review. *Adv. Mater.* **21**, 2741-2761, (2009).
- 165 Shirota, Y. & Kageyama, H. Charge carrier transporting molecular materials and their applications in devices. *Chem. Rev.* **107**, 953-1010, (2007).
- 166 Schwartz, B. J. Conjugated polymers as molecular materials: How chain conformation and film morphology influence energy transfer and interchain interactions. *Annu. Rev. Phys. Chem.* **54**, 141-172, (2003).
- 167 Zheng, C. *et al.* Relationships between main-chain chirality and photophysical properties in chiral conjugated polymers. *J. Mater. Chem. C* **2**, 7336-7347, (2014).
- 168 Amabilino, D. B. in *Chirality in Supramolecular Assemblies: Causes and Consequences* (ed Richard F. Keene) Ch. 6. Chiral influences in functional molecular materials, (John Wiley & Sons, Ltd., 2017).
- 169 Liu, M., Zhang, L. & Wang, T. Supramolecular chirality in self-assembled systems. *Chem. Rev.* **115**, 7304-7397, (2015).
- 170 Miyake, J., Tsuji, Y., Nagai, A. & Chujo, Y. Nanofiber formation via the self-assembly of a chiral regioregular poly(azomethine). *Chem. Commun.*, 2183-2185, (2009).
- 171 Dai, X. M., Goto, H., Akagi, K. & Shirakawa, H. Synthesis and properties of novel ferroelectric liquid crystalline polyacetylene derivatives. *Synth. Met.* **102**, 1289-1290, (1999).
- 172 Larossi, D. *et al.* Synthesis and spectroscopic and electrochemical characterisation of a conducting polythiophene bearing a chiral β -substituent: Polymerisation of (+)-4,4'-bis[(S)-2-methylbutylsulfanyl]-2,2'-bithiophene. *Chem. Eur. J.* **7**, 676-685, (2001).
- 173 Zou, W. *et al.* Biomimetic superhelical conducting microfibers with homochirality for enantioselective sensing. *J. Am. Chem. Soc.* **136**, 578-581, (2014).
- 174 Yan, Y., Fang, J., Liang, J., Zhang, Y. & Wei, Z. Helical heterojunctions originating from helical inversion of conducting polymer nanofibers. *Chem. Commun.* **48**, 2843-2845, (2012).
- 175 Weng, S., Lin, Z., Chen, L. & Zhou, J. Electrochemical synthesis and optical properties of helical polyaniline nanofibers. *Electrochim. Acta* **55**, 2727-2733, (2010).
- 176 Yan, Y., Yu, Z., Huang, Y. W., Yuan, W. X. & Wei, Z. X. Helical polyaniline nanofibers induced by chiral dopants by a polymerization process. *Adv. Mater.* **19**, 3353-3357, (2007).
- 177 Tao, Y. *et al.* Hierarchical self-assembly of hexagonal single-crystal nanosheets into 3D layered superlattices with high conductivity. *Nanoscale* **4**, 3729-3733, (2012).
- 178 Yan, Y., Wang, R., Qiu, X. & Wei, Z. Hexagonal superlattice of chiral conducting polymers self-assembled by mimicking β -sheet proteins with anisotropic electrical transport. *J. Am. Chem. Soc.* **132**, 12006-12012, (2010).
- 179 Arias, S., Freire, F., Quiñoá, E. & Riguera, R. Nanospheres, nanotubes, toroids, and gels with controlled macroscopic chirality. *Angew. Chem. Int. Ed.* **53**, 13720-13724, (2014).
- 180 Zhang, C., Li, M., Lu, H.-Y. & Chen, C.-F. Synthesis, chiroptical properties, and self-assembled nanoparticles of chiral conjugated polymers based on optically stable helical aromatic esters. *RSC Adv.* **8**, 1014-1021, (2018).
- 181 Pleus, S. & Schulte, B. Poly(pyrroles) containing chiral side chains: effect of substituents on the chiral recognition in the doped as well as in the undoped state of the polymer film. *J. Solid State Electrochem.* **5**, 522-530, (2001).
- 182 Fronk, S. L. *et al.* Chiroptical properties of a benzotriazole-thiophene copolymer bearing chiral ethylhexyl side chains. *Macromolecules* **49**, 9301-9308, (2016).
- 183 Fronk, S. L. *et al.* Effect of chiral 2-ethylhexyl side chains on chiroptical properties of the narrow bandgap conjugated polymers PCPDTBT and PCDTPT. *Chem. Sci.* **7**, 5313-5321, (2016).

- 184 Pauling, L., Corey, R. B. & Branson, H. R. The structure of proteins: Two hydrogen-bonded helical configurations of the polypeptide chain. *Proc. Natl. Acad. Sci. U. S. A.* **37**, 205-211, (1951).
- 185 Watson, J. D. & Crick, F. H. C. Molecular structure of nucleic acids: A structure for deoxyribose nucleic acid. *Nature* **171**, 737, (1953).
- 186 Nakano, T. & Okamoto, Y. Synthetic helical polymers: Conformation and function. *Chem. Rev.* **101**, 4013-4038, (2001).
- 187 Yashima, E. *et al.* Supramolecular helical systems: Helical assemblies of small molecules, foldamers, and polymers with chiral amplification and their functions. *Chem. Rev.* **116**, 13752-13990, (2016).
- 188 Yashima, E., Maeda, K., Iida, H., Furusho, Y. & Nagai, K. Helical polymers: synthesis, structures, and functions. *Chem. Rev.* **109**, 6102-6211, (2009).
- 189 Christofferson, A. J. *et al.* Molecular mapping of poly(methyl methacrylate) super-helix stereocomplexes. *Chem. Sci.* **6**, 1370-1378, (2015).
- 190 Kawauchi, T., Kitaura, A., Kumaki, J., Kusanagi, H. & Yashima, E. Helix-sense-controlled synthesis of optically active poly(methyl methacrylate) stereocomplexes. *J. Am. Chem. Soc.* **130**, 11889-11891, (2008).
- 191 Nolte, R. J. M., Van Beijnen, A. J. M. & Drenth, W. Chirality in polyisocyanides. *J. Am. Chem. Soc.* **96**, 5932-5933, (1974).
- 192 Green, M. M. *et al.* Macromolecular stereochemistry: The out-of-proportion influence of optically active comonomers on the conformational characteristics of polyisocyanates. The sergeants and soldiers experiment. *J. Am. Chem. Soc.* **111**, 6452-6454, (1989).
- 193 Green, M. M. *et al.* Majority rules in the copolymerization of mirror-image isomers. *J. Am. Chem. Soc.* **117**, 4181-4182, (1995).
- 194 Okamoto, Y., Nakano, T., Habaue, S., Shiohara, K. & Maeda, K. Synthesis and chiral recognition of helical polymers. *J. Macromol. Sci. A.* **A34**, 1771-1783, (1997).
- 195 Song, C., Zhang, C. H., Wang, F. J., Yang, W. T. & Deng, J. P. Chiral polymeric microspheres grafted with optically active helical polymer chains: A new class of materials for chiral recognition and chirally controlled release. *Polym. Chem.* **4**, 645-652, (2013).
- 196 Tamura, K., Miyabe, T., Iida, H. & Yashima, E. Separation of enantiomers on diastereomeric right- and left-handed helical poly(phenyl isocyanide)s bearing L-alanine pendants immobilized on silica gel by HPLC. *Polym. Chem.* **2**, 91-98, (2011).
- 197 Liu, L. *et al.* New achiral phenylacetylene monomers having an oligosiloxanyl group most suitable for helix-sense-selective polymerization and for obtaining good optical resolution membrane materials. *Macromolecules* **43**, 9268-9276, (2010).
- 198 Nakano, T., Satoh, Y. & Okamoto, Y. Synthesis and chiral recognition ability of a cross-linked polymer gel prepared by a molecular imprint method using chiral helical polymers as templates. *Macromolecules* **34**, 2405-2407, (2001).
- 199 Miyabe, T., Iida, H., Ohnishi, A. & Yashima, E. Enantioseparation on poly(phenyl isocyanide)s with macromolecular helicity memory as chiral stationary phases for HPLC. *Chem. Sci.* **3**, 863-867, (2012).
- 200 Okamoto, Y. Precision synthesis, structure and function of helical polymers. *Proc. Jpn. Acad., Ser. B* **91**, 246-261, (2015).
- 201 Okamoto, Y. *et al.* Novel packing material for optical resolution: (+)-poly(triphenylmethyl methacrylate) coated on macroporous silica gel. *J. Am. Chem. Soc.* **103**, 6971-6973, (1981).
- 202 Yuki, H., Okamoto, Y. & Okamoto, I. Resolution of racemic compounds by optically active poly(triphenylmethyl methacrylate). *J. Am. Chem. Soc.* **102**, 6356-6358, (1980).
- 203 Maeda, K. & Yashima, E. Helical polyacetylenes induced via noncovalent chiral interactions and their applications as chiral materials. *Top. Curr. Chem.* **375**, 72, (2017).

- 204 Shimomura, K., Ikai, T., Kanoh, S., Yashima, E. & Maeda, K. Switchable enantioseparation based on macromolecular memory of a helical polyacetylene in the solid state. *Nature Chem.* **6**, 429, (2014).
- 205 Yamamoto, T., Murakami, R., Komatsu, S. & Suginome, M. Chirality-amplifying, dynamic induction of single-handed helix by chiral guests to macromolecular chiral catalysts bearing boronyl pendants as receptor sites. *J. Am. Chem. Soc.* **140**, 3867-3870, (2018).
- 206 Reggelin, M., Doerr, S., Klusmann, M., Schultz, M. & Holbach, M. Helically chiral polymers: a class of ligands for asymmetric catalysis. *Proc. Natl. Acad. Sci. U. S. A.* **101**, 5461-5466, (2004).
- 207 Yoshinaga, Y., Yamamoto, T. & Suginome, M. Chirality-switchable 2,2'-bipyridine ligands attached to helical poly(quinoxaline-2,3-diyl)s for copper-catalyzed asymmetric cyclopropanation of alkenes. *ACS Macro Lett.* **6**, 705-710, (2017).
- 208 Zhou, L. *et al.* Significant improvement on enantioselectivity and diastereoselectivity of organocatalyzed asymmetric aldol reaction using helical polyisocyanides bearing proline pendants. *ACS Macro Lett.* **6**, 824-829, (2017).
- 209 Zhang, H. Y., Yang, W. T. & Deng, J. P. Optically active helical polymers with pendent thiourea groups: Chiral organocatalyst for asymmetric michael addition reaction. *J. Polym. Sci., Part A: Polym. Chem.* **53**, 1816-1823, (2015).
- 210 Zhang, D., Ren, C., Yang, W. & Deng, J. Helical polymer as mimetic enzyme catalyzing asymmetric aldol reaction. *Macromol. Rapid Commun.* **33**, 652-657, (2012).
- 211 Tang, Z. L., Iida, H., Hu, H. Y. & Yashima, E. Remarkable enhancement of the enantioselectivity of an organocatalyzed asymmetric Henry reaction assisted by helical poly(phenylacetylene)s bearing cinchona alkaloid pendants via an amide linkage. *ACS Macro Lett.* **1**, 261-265, (2012).
- 212 Yamamoto, T., Murakami, R. & Suginome, M. Single-handed helical poly(quinoxaline-2,3-diyl)s bearing achiral 4-aminopyrid-3-yl pendants as highly enantioselective, reusable chiral nucleophilic organocatalysts in the Steglich reaction. *J. Am. Chem. Soc.* **139**, 2557-2560, (2017).
- 213 Miyabe, T., Hase, Y., Iida, H., Maeda, K. & Yashima, E. Synthesis of functional poly(phenyl isocyanide)s with macromolecular helicity memory and their use as asymmetric organocatalysts. *Chirality* **21**, 44-50, (2009).
- 214 Cornelissen, J. J. *et al.* β -Helical polymers from isocyanopeptides. *Science* **293**, 676-680, (2001).
- 215 Mayer, S. & Zentel, R. Switching of the helical polymer conformation in a solid polymer film. *Macromol. Rapid Commun.* **21**, 927-930, (2000).
- 216 Ohira, A. *et al.* Versatile helical polymer films: chiroptical inversion switching and memory with re-writable (RW) and write-once read-many (WORM) modes. *Adv. Mater.* **16**, 1645-1650, (2004).
- 217 Ousaka, N., Mamiya, F., Iwata, Y., Nishimura, K. & Yashima, E. "Helix-in-helix" superstructure formation through encapsulation of fullerene-bound helical peptides within a helical poly(methyl methacrylate) cavity. *Angew. Chem. Int. Ed.* **56**, 791-795, (2016).
- 218 Furusho, Y. & Yashima, E. Development of synthetic double helical polymers and oligomers. *J. Polym. Sci., Part A: Polym. Chem.* **47**, 5195-5207, (2009).
- 219 Kumaki, J., Kawauchi, T., Okoshi, K., Kusanagi, H. & Yashima, E. Supramolecular helical structure of the stereocomplex composed of complementary isotactic and syndiotactic poly(methyl methacrylate)s as revealed by atomic force microscopy. *Angew. Chem. Int. Ed.* **46**, 5348-5351, (2007).
- 220 Kumaki, J., Kawauchi, T., Ute, K., Kitayama, T. & Yashima, E. Molecular weight recognition in the multiple-stranded helix of a synthetic polymer without specific monomer-monomer interaction. *J. Am. Chem. Soc.* **130**, 6373-6380, (2008).

- 221 Ren, J. M. *et al.* Controlled formation and binding selectivity of discrete oligo(methyl methacrylate) stereocomplexes. *J. Am. Chem. Soc.* **140**, 1945-1951, (2018).
- 222 Semegen, S. T. in *Encyclopedia of Physical Science and Technology (3rd Edition)* (ed Robert A Meyers) Ch. Rubber, natural 381-394 (Academic Press, 2003).
- 223 Mark, J. E. *Polymer Data Handbook*. 2nd edn, (Oxford University Press, 2009).
- 224 Porri, L. & Giarrusso, A. in *Comprehensive Polymer Science and Supplements* (ed John C. Bevington) Ch. 5 Conjugated diene polymerization, 53-108 (Pergamon, 1989).
- 225 Phuphuak, Y., Bonnet, F., Stoclet, G., Bria, M. & Zinck, P. Isoprene chain shuttling polymerisation between cis and trans regulating catalysts: Straightforward access to a new material. *Chem. Commun.* **53**, 5330-5333, (2017).
- 226 Tanaka, R. *et al.* Synthesis of stereodiblock polyisoprene consisting of cis-1,4 and trans-1,4 sequences by using a neodymium catalyst: change of the stereospecificity triggered by an aluminum compound. *Polym. Chem.* **7**, 1239-1243, (2016).
- 227 Ricci, G., Leone, G., Boglia, A., Boccia, A. C. & Zetta, L. Cis-1,4-alt-3,4 polyisoprene: Synthesis and characterization. *Macromolecules* **42**, 9263-9267, (2009).
- 228 Annunziata, L., Duc, M. & Carpentier, J.-F. Chain growth polymerization of isoprene and stereoselective isoprene–styrene copolymerization promoted by an ansa-bis(indenyl)allyl–yttrium complex. *Macromolecules* **44**, 7158-7166, (2011).
- 229 Zhang, X., Zhang, C., Wang, Y. & Li, Y. Synthesis and characterization of symmetrical triblock copolymers containing crystallizable high-trans-1,4-polybutadiene. *Polym. Bull. (Berlin)* **65**, 201-213, (2010).
- 230 Bunn, C. W. Molecular structure and rubber-like elasticity - III. Molecular movements in rubber-like polymers. *Proc. R. Soc. London, A* **180**, 82-99, (1942).
- 231 Bunn, C. W. Molecular structure and rubber-like elasticity I. The crystal structures of β gutta-percha, rubber and polychloroprene. *Proc. R. Soc. London, A* **180**, 40-66, (1942).
- 232 MacGregor, E. A. in *Encyclopedia of Physical Science and Technology (3rd Edition)* (ed A. Robert Meyers) Ch. Biopolymers 207-245 (Academic Press, 2003).
- 233 Nie, Y., Gu, Z., Wei, Y., Hao, T. & Zhou, Z. Features of strain-induced crystallization of natural rubber revealed by experiments and simulations. *Polym. J.* **49**, 309, (2017).
- 234 Huneau, B. Strain-induced crystallisation of natural rubber: A review of X-ray diffraction investigations. *Rubber Chem. Technol.* **84**, 425-452, (2011).
- 235 Coran, A. Y. in *The Science and Technology of Rubber (4th Edition)* (eds James E. Mark, Burak Erman, & C. Michael Roland) Ch. 7. Vulcanization, 337-381 (Academic Press, 2013).
- 236 Semegen, S. T. in *Encyclopedia of Physical Science and Technology (3rd Edition)* (ed Robert A Meyers) Ch. Rubber, synthetic, 395-405 (Academic Press, 2003).
- 237 Aufdermarsh, C. A. & Pariser, R. cis-polychloroprene. *Journal of Polymer Science Part A: General Papers* **2**, 4727-4733, (1964).
- 238 Ricci, G. & Leone, G. Recent advances in the polymerization of butadiene over the last decade. *Polyolefins Journal* **1**, 43-60, (1999).
- 239 Kuntz, I. & Gerber, A. The butyllithium-initiated polymerization of 1,3-butadiene. *J. Polym. Sci.* **42**, 299-308, (1960).
- 240 Rodgers, B. & Waddell, W. in *The Science and Technology of Rubber (4th Edition)* Ch. 9. The science of rubber compounding, 417-471 (Academic Press, 2013).
- 241 Laur, E., Kirillov, E. & Carpentier, J.-F. Engineering of syndiotactic and isotactic polystyrene-based copolymers via stereoselective catalytic polymerization. *Molecules* **22**, (2017).
- 242 Guo, F., Meng, R., Li, Y. & Hou, Z. Highly cis-1,4-selective terpolymerization of 1,3-butadiene and isoprene with styrene by a C₅H₅-ligated scandium catalyst *Polymer* **76**, 159-167, (2015).
- 243 Jian, Z., Tang, S. & Cui, D. Highly regio- and stereoselective terpolymerization of styrene, isoprene and butadiene with lutetium-based coordination catalyst. *Macromolecules* **44**, 7675-7681, (2011).

- 244 Milione, S. *et al.* Stereoselective polymerization of conjugated dienes and styrene–butadiene copolymerization promoted by octahedral titanium catalyst. *Macromolecules* **40**, 5638–5643, (2007).
- 245 Ban, H. T. *et al.* A new approach to styrenic thermoplastic elastomers: Synthesis and characterization of crystalline styrene–butadiene–styrene triblock copolymers. *Macromolecules* **39**, 171–176, (2006).
- 246 Caprio, M., Serra, M. C., Bowen, D. E. & Grassi, A. Structural characterization of novel styrene–butadiene block copolymers containing syndiotactic styrene homosequences. *Macromolecules* **35**, 9315–9322, (2002).
- 247 Kaita, S., Hou, Z. & Wakatsuki, Y. Random- and block-copolymerization of 1,3-butadiene with styrene based on the stereospecific living system: $(C_5Me_5)_2Sm(\mu-Me)_2AlMe_2/Al(i-Bu)_3/[Ph_3C][B(C_6F_5)_4]^1$. *Macromolecules* **34**, 1539–1541, (2001).
- 248 Zambelli, A., Caprio, M., Grassi, A. & Bowen, D. E. Syndiotactic styrene-butadiene block copolymers synthesized with $CpTiX_3/MAO$ ($Cp = C_5H_5$, $X = Cl, F$; $Cp = C_5Me_5$, $X = Me$) and TiX_n/MAO ($n = 3$, $X = acac$; $n = 4$, $X = O\text{-tert-Bu}$). *Macromol. Chem. Phys.* **201**, 393–400, (2000).
- 249 C., K. H., G., F. M. & Barry, S. K. Click chemistry: Diverse chemical function from a few good reactions. *Angew. Chem. Int. Ed.* **40**, 2004–2021, (2001).
- 250 Lowe, A. B. Thiol-yne ‘click’/coupling chemistry and recent applications in polymer and materials synthesis and modification. *Polymer* **55**, 5517–5549, (2014).
- 251 Yao, B., Sun, J., Qin, A. & Tang, B. Z. Thiol-yne click polymerization. *Chin. Sci. Bull.* **58**, 2711–2718, (2013).
- 252 Lowe, A. B., Hoyle, C. E. & Bowman, C. N. Thiol-yne click chemistry: A powerful and versatile methodology for materials synthesis. *J. Mater. Chem.* **20**, 4745–4750, (2010).
- 253 Richard, H. Thiol-yne chemistry: A powerful tool for creating highly functional materials. *Angew. Chem. Int. Ed.* **49**, 3415–3417, (2010).
- 254 Liu, J., Lam, J. W. Y. & Tang, B. Z. Acetylenic polymers: Syntheses, structures, and functions. *Chem. Rev.* **109**, 5799–5867, (2009).
- 255 Di Giuseppe, A. *et al.* Ligand-controlled regioselectivity in the hydrothiolation of alkynes by rhodium N-heterocyclic carbene catalysts. *J. Am. Chem. Soc.* **134**, 8171–8183, (2012).
- 256 Liu, J. *et al.* Thiol-yne click polymerization: Regio- and stereoselective synthesis of sulfur-rich acetylenic polymers with controllable chain conformations and tunable optical properties. *Macromolecules* **44**, 68–79, (2011).
- 257 Nair, D. P. *et al.* The thiol-michael addition click reaction: A powerful and widely used tool in materials chemistry. *Chem. Mater.* **26**, 724–744, (2014).
- 258 Truong Vinh, X. & Dove Andrew, P. Organocatalytic, regioselective nucleophilic “click” addition of thiols to propiolic acid esters for polymer–polymer coupling. *Angew. Chem. Int. Ed.* **52**, 4132–4136, (2013).
- 259 Bell, C. A. *et al.* Independent control of elastomer properties through stereocontrolled synthesis. *Angew. Chem. Int. Ed.* **55**, 13076–13080, (2016).
- 260 Kuroda, H., Tomita, I. & Endo, T. A novel phosphine-catalysed polyaddition of terminal acetylenes bearing electron-withdrawing groups with dithiols. Synthesis of polymers having dithioacetal moieties in the main chain. *Polymer* **38**, 6049–6054, (1997).
- 261 W., J. C. K. *et al.* Metal-free alkyne polyhydrothiolation: Synthesis of functional poly(vinylenesulfide)s with high stereoregularity by regioselective thioclick polymerization. *Adv. Funct. Mater.* **20**, 1319–1328, (2010).
- 262 Gunay, U. S. *et al.* Ultrafast and efficient aza- and thiol-Michael reactions on a polyester scaffold with internal electron deficient triple bonds. *Polym. Chem.* **9**, 3037–3054, (2018).
- 263 Shi, Y. *et al.* Phenol-yne click polymerization: An efficient technique to facilely access regio- and stereoregular poly(vinylene ether ketone)s. *Chem. Eur. J.* **23**, 10725–10731, (2017).

- 264 Yao, B. *et al.* Catalyst-free thiol–yne click polymerization: A powerful and facile tool for preparation of functional poly(vinylene sulfide)s. *Macromolecules* **47**, 1325-1333, (2014).
- 265 He, B. *et al.* Spontaneous amino-yne click polymerization: A powerful tool toward regio- and stereospecific poly(β -aminoacrylate)s. *J. Am. Chem. Soc.* **139**, 5437-5443, (2017).
- 266 He, B., Wu, Y., Qin, A. & Tang, B. Z. Copper-catalyzed electrophilic polyhydroamination of internal alkynes. *Macromolecules* **50**, 5719-5728, (2017).
- 267 He, B. *et al.* Cu(I)-catalyzed amino-yne click polymerization. *Polym. Chem.* **7**, 7375-7382, (2016).
- 268 Deng, H. *et al.* Construction of regio- and stereoregular poly(enaminone)s by multicomponent tandem polymerizations of diynes, diacyl chloride and primary amines. *Polym. Chem.* **6**, 4436-4446, (2015).
- 269 Deng, H., He, Z., Lam, J. W. Y. & Tang, B. Z. Regio- and stereoselective construction of stimuli-responsive macromolecules by a sequential coupling-hydroamination polymerization route. *Polym. Chem.* **6**, 8297-8305, (2015).
- 270 Sutthasupa, S., Shiotsuki, M. & Sanda, F. Recent advances in ring-opening metathesis polymerization, and application to synthesis of functional materials. *Polym. J.* **42**, 905, (2010).
- 271 Bielawski, C. W. & Grubbs, R. H. Living ring-opening metathesis polymerization. *Prog. Polym. Sci.* **32**, 1-29, (2007).
- 272 Brydson, J. A. in *Plastics Materials (7th Edition)* Ch. 11. Aliphatic polyolefins other than polyethylene, and diene rubbers, 247-310 (Butterworth-Heinemann, 1999).
- 273 Mane, S. R., Sathyan, A. & Shunmugam, R. Synthesis of norbornene derived helical copolymer by simple molecular marriage approach to produce smart nanocarrier. *Sci. Rep.* **7**, 44857, (2017).
- 274 Autenrieth, B. & Schrock, R. R. Stereospecific ring-opening metathesis polymerization (ROMP) of norbornene and tetracyclododecene by Mo and W initiators. *Macromolecules* **48**, 2493-2503, (2015).
- 275 Schrock, R. R. Synthesis of stereoregular ROMP polymers using molybdenum and tungsten imido alkylidene initiators. *Dalton Trans.* **40**, 7484-7495, (2011).
- 276 Ahmed, S., Bidstrup Sue, A., Kohl, P. & Ludovice, P. Stereochemical structure-property relationships in polynorbornene from simulation. *Macromol. Symp.* **133**, 1-10, (1998).
- 277 Chiang, C. K. *et al.* Electrical conductivity in doped polyacetylene. *Phys. Rev. Lett.* **39**, 1098-1101, (1977).
- 278 Shirakawa, H., Ito, T. & Ikeda, S. Electrical properties of polyacetylene with various cis-trans compositions. *Die Makromolekulare Chemie* **179**, 1565-1573, (1978).
- 279 MacDiarmid, A. G. & Heeger, A. J. Organic metals and semiconductors: The chemistry of polyacetylene, (CH)_x, and its derivatives. *Synth. Met.* **1**, 101-118, (1980).
- 280 Basescu, N. *et al.* High electrical conductivity in doped polyacetylene. *Nature* **327**, 403, (1987).
- 281 Likhtenshtein, G. in *Stilbenes: Applications in Chemistry, Life Sciences and Materials Science* (ed G. Likhtenshtein) Ch. 6. Stilbene materials, (WILEY-VCH Verlag GmbH & Co. KGaA, 2009).
- 282 Waldeck, D. H. Photoisomerization dynamics of stilbenes. *Chem. Rev.* **91**, 415-436, (1991).
- 283 Bourgeaux, M. & Skene, W. G. A highly conjugated p- and n-type polythiophenoazomethine: Synthesis, spectroscopic, and electrochemical investigation. *Macromolecules* **40**, 1792-1795, (2007).
- 284 Skene, W. G. & Dufresne, S. Easy one-pot synthesis of energy transfer cassettes. *Org. Lett.* **6**, 2949-2952, (2004).
- 285 Thomas, O., Inganäs, O. & Andersson, M. R. Synthesis and properties of a soluble conjugated poly(azomethine) with high molecular weight. *Macromolecules* **31**, 2676-2678, (1998).
- 286 Yang, C.-J. & Jenekhe, S. A. Conjugated aromatic polyimines. 2. Synthesis, structure, and properties of new aromatic polyazomethines. *Macromolecules* **28**, 1180-1196, (1995).

- 287 Yang, C. J. & Jenekhe, S. A. Conjugated aromatic poly(azomethines). 1. Characterization of structure, electronic spectra, and processing of thin films from soluble complexes. *Chem. Mater.* **3**, 878-887, (1991).
- 288 Miyake, J. & Chujo, Y. Aza-wittig polymerization: A simple method for the synthesis of regioregular poly(azomethine)s. *Macromolecules* **41**, 9677-9682, (2008).
- 289 Guarín, S. A. P., Bourgeaux, M., Dufresne, S. & Skene, W. G. Photophysical, crystallographic, and electrochemical characterization of symmetric and unsymmetric self-assembled conjugated thiopheno azomethines. *J. Org. Chem.* **72**, 2631-2643, (2007).
- 290 Berti, C. *et al.* Bio-based terephthalate polyesters. US2010168373 (A1) (2015).
- 291 Wang, J. *et al.* Modification of poly(ethylene 2,5-furandicarboxylate) (PEF) with 1, 4-cyclohexanedimethanol: Influence of stereochemistry of 1,4-cyclohexylene units. *Polymer* **137**, 173-185, (2018).
- 292 Bert, V., Bart, R., Rudolph, W., Monique, B. & E., K. C. Influence of stereochemistry on the thermal properties of partially cycloaliphatic polyamides. *J. Polym. Sci., Part A: Polym. Chem.* **40**, 1962-1971, (2002).
- 293 Annamaria, C. *et al.* Effect of 1,4-cyclohexylene units on thermal properties of poly(1,4-cyclohexylenedimethylene adipate) and similar aliphatic polyesters. *Polym. Int.* **62**, 1210-1217, (2013).
- 294 Celli, A., Marchese, P., Sullalti, S., Berti, C. & Barbiroli, G. Eco-friendly poly(butylene 1,4-cyclohexanedicarboxylate): Relationships between stereochemistry and crystallization behavior. *Macromol. Chem. Phys.* **212**, 1524-1534, (2011).
- 295 Berti, C. *et al.* Environmentally friendly copolyesters containing 1,4-cyclohexane dicarboxylate units, 1-relationships between chemical structure and thermal properties. *Macromol. Chem. Phys.* **211**, 1559-1571, (2010).
- 296 Berti, C. *et al.* Poly(1,4-cyclohexylenedimethylene 1,4-cyclohexanedicarboxylate): Influence of stereochemistry of 1,4-cyclohexylene units on the thermal properties. *J. Polym. Sci., Part B: Polym. Phys.* **46**, 619-630, (2008).
- 297 Berti, C. *et al.* Influence of molecular structure and stereochemistry of the 1,4-cyclohexylene ring on thermal and mechanical behavior of poly(butylene 1,4-cyclohexanedicarboxylate). *Macromol. Chem. Phys.* **209**, 1333-1344, (2008).
- 298 Liu, F. *et al.* Role of cis-1,4-cyclohexanedicarboxylic acid in the regulation of the structure and properties of a poly(butylene adipate-co-butylene 1,4-cyclohexanedicarboxylate) copolymer. *RSC Adv.* **6**, 65889-65897, (2016).
- 299 Galbis, J. A., García-Martín, M. d. G., de Paz, M. V. & Galbis, E. Synthetic polymers from sugar-based monomers. *Chem. Rev.* **116**, 1600-1636, (2016).
- 300 Marcus, R. & Regina, P. Isosorbide as a renewable platform chemical for versatile applications—quo vadis? *ChemSusChem* **5**, 167-176, (2012).
- 301 Fenouillot, F., Rousseau, A., Colomines, G., Saint-Loup, R. & Pascault, J. P. Polymers from renewable 1,4:3,6-dianhydrohexitols (isosorbide, isomannide and isoidide): A review. *Prog. Polym. Sci.* **35**, 578-622, (2010).
- 302 Nôtre, J. L., Haveren, J. v. & Es, D. S. v. Synthesis of isoidide through epimerization of isosorbide using ruthenium on carbon. *ChemSusChem* **6**, 693-700, (2013).
- 303 Dillon, G. P. *et al.* Isosorbide-based cholinesterase inhibitors; replacement of 5-ester groups leading to increased stability. *Bioorg. Med. Chem.* **18**, 1045-1053, (2010).
- 304 Dillon, G. *The synthesis and biological evaluation of a novel class of butyrylcholinesterase inhibitors using isosorbide as a building block* Ph.D thesis, Trinity College, Dublin, Ireland, (2007).
- 305 Cope, A. C. & Shen, T. Y. The stereochemistry of 1,4: 3,6-dianhydrohexitol derivatives. *J. Am. Chem. Soc.* **78**, 3177-3182, (1956).
- 306 Thiem, J. & Bachmann, F. Synthesis and properties of polyamides derived from anhydro- and dianhydroalditols. *Die Makromolekulare Chemie* **192**, 2163-2182, (1991).

- 307 Rajput, B. S., Gaikwad, S. R., Menon, S. K. & Chikkali, S. H. Sustainable polyacetals from isohexides. *Green Chem.* **16**, 3810-3818, (2014).
- 308 Wu, J. *et al.* Fully isohexide-based polyesters: synthesis, characterization, and structure–properties relations. *Macromolecules* **46**, 384-394, (2013).
- 309 Reinhard, S., Matthias, R. & Matthias, B. Synthesis and properties of high-molecular-weight polyesters based on 1,4:3,6-dianhydrohexitols and terephthalic acid. *Die Makromolekulare Chemie* **194**, 53-64, (1993).
- 310 Bachmann, F., Reimer, J., Ruppenstein, M. & Thiem, J. Synthesis of novel polyurethanes and polyureas by polyaddition reactions of dianhydrohexitol configured diisocyanates. *Macromol. Chem. Phys.* **202**, 3410-3419, (2001).
- 311 Zenner, M. D., Xia, Y., Chen, J. S. & Kessler, M. R. Polyurethanes from isosorbide-based diisocyanates. *ChemSusChem* **6**, 1182-1185, (2013).
- 312 Hashimoto, K., Wibullucksanakul, S., Matsuura, M. & Okada, M. Macromolecular synthesis from saccharic lactones. Ring-opening polyaddition of D-glucaro- and D-mannaro-1,4:6,3-dilactones with alkylenediamines. *J. Polym. Sci., Part A: Polym. Chem.* **31**, 3141-3149, (1993).
- 313 Raytchev Pascal, D. *et al.* 1,4:3,6-Dianhydrohexitols: Original platform for the design of biobased polymers using robust, efficient, and orthogonal chemistry. *Pure Appl. Chem.* **85**, 511, (2012).
- 314 Besset, C., Pascault, J.-P., Fleury, E., Drockenmuller, E. & Bernard, J. Structure–properties relationship of biosourced stereocontrolled polytriazoles from click chemistry step growth polymerization of diazide and dialkyne dianhydrohexitols. *Biomacromolecules* **11**, 2797-2803, (2010).
- 315 Kieber, R. J., Silver, S. A. & Kennemur, J. G. Stereochemical effects on the mechanical and viscoelastic properties of renewable polyurethanes derived from isohexides and hydroxymethylfurfural. *Polym. Chem.*, (2017).
- 316 Feng, X., East, A. J., Hammond, W. & Jaffe, M. in *Contemporary Science of Polymeric Materials* Vol. 1061 *ACS Symposium Series* Ch. 1. Sugar-based chemicals for environmentally sustainable applications, 3-27 (American Chemical Society, 2010).
- 317 Thiagarajan, S. *et al.* Isohexide hydroxy esters: synthesis and application of a new class of biobased AB-type building blocks. *RSC Adv.* **4**, 47937-47950, (2014).
- 318 Lillie, L. M., Tolman, W. B. & Reineke, T. M. Degradable and renewably-sourced poly(ester-thioethers) by photo-initiated thiol–ene polymerization. *Polym. Chem.* **9**, 3272-3278, (2018).
- 319 Wilbon, P. A. *et al.* Degradable thermosets erived from an isosorbide/succinic anhydride monomer and glycerol. *ACS Sustainable Chem. Eng.* **5**, 9185-9190, (2017).
- 320 Shearouse, W. C., Lillie, L. M., Reineke, T. M. & Tolman, W. B. Sustainable polyesters derived from glucose and castor oil: Building block structure impacts properties. *ACS Macro Lett.* **4**, 284-288, (2015).
- 321 Gallagher, J. J., Hillmyer, M. A. & Reineke, T. M. Degradable thermosets from sugar-derived dilactones. *Macromolecules* **47**, 498-505, (2014).
- 322 Fuoss, R. M. & Sadek, H. Mutual interaction of polyelectrolytes. *Science* **110**, 552, (1949).
- 323 Liquori, A. M. *et al.* Complementary stereospecific interaction between isotactic and syndiotactic polymer molecules. *Nature* **206**, 358, (1965).
- 324 Watanabe, W. H., Ryan, C. F., Fleischer, P. C. & Garrett, B. S. Measurement of the tacticity of syndiotactic poly-(methylmethacrylate) by the gel melting point. *J. Phys. Chem.* **65**, 896-896, (1961).
- 325 Xie, Q., Yu, C. & Pan, P. in *Crystallization in Multiphase Polymer Systems* (eds Mohammed Arif P, E. Bhoje Gowd, & Nandakumar Kalarikkal) Ch. 17. Stereocomplex crystallization of polymers with complementary configurations, 535-573 (Elsevier, 2018).
- 326 Slager, J. & Domb, A. J. Biopolymer stereocomplexes. *Adv. Drug Delivery Rev.* **55**, 549-583, (2003).

- 327 Hatada, K. & Kitayama, T. Structurally controlled polymerizations of methacrylates and acrylates. *Polym. Int.* **49**, 11-47, (2000).
- 328 Spěváček, J. & Schneider, B. Aggregation of stereoregular poly(methyl methacrylates). *Adv. Colloid Interface Sci.* **27**, 81-150, (1987).
- 329 Miyamoto, T. & Inagaki, H. The stereocomplex formation in poly(methyl methacrylate) and the stereospecific polymerization of its monomer. *Polym. J.* **1**, 46, (1970).
- 330 Yu, J. M., Yu, Y.-S., Dubois, P. & Jerome, R. Stereocomplexation of sPMMA-PBD-sPMMA triblock copolymers with isotactic PMMA: 1. Thermal and mechanical properties of stereocomplexes. *Polymer* **38**, 2143-2154, (1997).
- 331 Yu, Y. S., Dubois, P., Jérôme, R. & Teyssié, P. Difunctional initiator based on 1,3-diisopropenylbenzene. IV. Synthesis and modification of poly(alkyl methacrylate-*b*-styrene-*b*-butadiene-*b*-styrene-*b*-alkyl methacrylate (MSBSM)) thermoplastic elastomers. *J. Polym. Sci., Part A: Polym. Chem.* **34**, 2221-2228, (1996).
- 332 Deuring, H., Alberda van Ekenstein, G. O. R., Challa, G., Mason, J. P. & Hogen-Esch, T. E. Stereocomplex formation in blends of block copolymers of syndiotactic poly(methyl methacrylate) (PMMA)-poly(dimethylsiloxane) (PDMS) and isotactic PMMA. Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). *Macromolecules* **28**, 1952-1958, (1995).
- 333 Berkoukchi, M. P., Hélary, G., Bélorgey, G. & Hogen-Esch, T. E. Stereocomplex formation in polybutadiene-syndiotactic poly(methyl methacrylate) block copolymers blended with isotactic poly(methyl methacrylate). *Polym. Bull. (Berlin)* **32**, 297-303, (1994).
- 334 Helary, G., Belorgey, G. & Hogen-Esch, T. E. Stereocomplex formation in polybutadiene-syndiotactic poly (methyl methacrylate) block copolymers blended with isotactic poly (methyl methacrylate). *Polymer* **33**, 1953-1958, (1992).
- 335 Kennedy, J. P., Price, J. L. & Koshimura, K. Novel thermoplastic elastomer triblocks of a soft polyisobutylene midblock connected to two hard PMMA stereocomplex outer blocks. *Macromolecules* **24**, 6567-6571, (1991).
- 336 Kitayama, T., Nishiura, T. & Hatada, K. PMMA-block-polyisobutylene-block-PMMA prepared with α,ω -dilithiated polyisobutylene and its characterization. *Polym. Bull. (Berlin)* **26**, 513-520, (1991).
- 337 Escudé, N. C., Ning, Y. & Chen, E. Y. X. In situ stereocomplexing polymerization of methyl methacrylate by diastereospecific metallocene catalyst pairs. *Polym. Chem.* **3**, 3247-3255, (2012).
- 338 Crne, M., Park, J. O. & Srinivasarao, M. Electrospinning physical gels: The case of stereocomplex PMMA. *Macromolecules* **42**, 4353-4355, (2009).
- 339 Kawauchi, T., Kumaki, J., Okoshi, K. & Yashima, E. Stereocomplex formation of isotactic and syndiotactic poly(methyl methacrylate)s in ionic liquids leading to thermoreversible ion gels. *Macromolecules* **38**, 9155-9160, (2005).
- 340 Kawauchi, T., Kumaki, J. & Yashima, E. Nanosphere and nanonetwork formations of [60]fullerene-end-capped stereoregular poly(methyl methacrylate)s through stereocomplex formation combined with self-assembly of the fullerenes. *J. Am. Chem. Soc.* **128**, 10560-10567, (2006).
- 341 Serizawa, T., Hamada, K.-i. & Akashi, M. Polymerization within a molecular-scale stereoregular template. *Nature* **429**, 52, (2004).
- 342 Goh, T. K. *et al.* Nano-to-macroscale poly(methyl methacrylate) stereocomplex assemblies. *Angew. Chem. Int. Ed.* **48**, 8707-8711, (2009).
- 343 Vidal, F., Falivene, L., Caporaso, L., Cavallo, L. & Chen, E. Y. X. Robust cross-linked stereocomplexes and C₆₀ inclusion complexes of vinyl-functionalized stereoregular polymers derived from chemo/stereoselective coordination polymerization. *J. Am. Chem. Soc.* **138**, 9533-9547, (2016).

- 344 Raquez, J.-M., Habibi, Y., Murariu, M. & Dubois, P. Polylactide (PLA)-based nanocomposites. *Prog. Polym. Sci.* **38**, 1504-1542, (2013).
- 345 Gao, C., Yu, L., Liu, H. & Chen, L. Development of self-reinforced polymer composites. *Prog. Polym. Sci.* **37**, 767-780, (2012).
- 346 Ikada, Y., Jamshidi, K., Tsuji, H. & Hyon, S. H. Stereocomplex formation between enantiomeric poly(lactides). *Macromolecules* **20**, 904-906, (1987).
- 347 Tsuji, H. & Ikada, Y. Stereocomplex formation between enantiomeric poly(lactic acid)s. XI. Mechanical properties and morphology of solution-cast films. *Polymer* **40**, 6699-6708, (1999).
- 348 Hirata, M. & Kimura, Y. Thermomechanical properties of stereoblock poly(lactic acid)s with different PLLA/PDLA block compositions. *Polymer* **49**, 2656-2661, (2008).
- 349 Pan, P. *et al.* Competitive stereocomplexation, homocrystallization, and polymorphic crystalline transition in poly(l-lactic acid)/poly(d-lactic acid) racemic blends: Molecular weight effects. *J. Phys. Chem. B.* **119**, 6462-6470, (2015).
- 350 Andersson, S. R., Hakkarainen, M., Inkinen, S., Södergård, A. & Albertsson, A.-C. Polylactide stereocomplexation leads to higher hydrolytic stability but more acidic hydrolysis product pattern. *Biomacromolecules* **11**, 1067-1073, (2010).
- 351 Anderson, K. S. & Hillmyer, M. A. Melt preparation and nucleation efficiency of polylactide stereocomplex crystallites. *Polymer* **47**, 2030-2035, (2006).
- 352 Tsuji, H., Takai, H. & Saha, S. K. Isothermal and non-isothermal crystallization behavior of poly(l-lactic acid): Effects of stereocomplex as nucleating agent. *Polymer* **47**, 3826-3837, (2006).
- 353 Xie, Q., Han, L., Shan, G., Bao, Y. & Pan, P. Polymorphic crystalline structure and crystal morphology of enantiomeric poly(lactic acid) blends tailored by a self-assemblable aryl amide nucleator. *ACS Sustainable Chem. Eng.* **4**, 2680-2688, (2016).
- 354 Han, L., Pan, P., Shan, G. & Bao, Y. Stereocomplex crystallization of high-molecular-weight poly(l-lactic acid)/poly(d-lactic acid) racemic blends promoted by a selective nucleator. *Polymer* **63**, 144-153, (2015).
- 355 Bao, R.-Y., Yang, W., Wei, X.-F., Xie, B.-H. & Yang, M.-B. Enhanced formation of stereocomplex crystallites of high molecular weight poly(l-lactide)/poly(d-lactide) blends from melt by using poly(ethylene glycol). *ACS Sustainable Chem. Eng.* **2**, 2301-2309, (2014).
- 356 Fukushima, K. & Kimura, Y. Stereocomplexed polylactides (Neo-PLA) as high-performance bio-based polymers: their formation, properties, and application. *Polym. Int.* **55**, 626-642, (2006).
- 357 Platel, R. H., Hodgson, L. M. & Williams, C. K. Biocompatible initiators for lactide polymerization. *Polym. Rev.* **48**, 11-63, (2008).
- 358 Lin, T., Liu, X.-Y. & He, C. Calculation of infrared/Raman spectra and dielectric properties of various crystalline poly(lactic acid)s by density functional perturbation theory (DFPT) method. *J. Phys. Chem. B.* **116**, 1524-1535, (2012).
- 359 Lin, T. T., Liu, X. Y. & He, C. A DFT study on poly(lactic acid) polymorphs. *Polymer* **51**, 2779-2785, (2010).
- 360 Tsuji, H. Poly(lactic acid) stereocomplexes: A decade of progress. *Adv. Drug Delivery Rev.* **107**, 97-135, (2016).
- 361 Tsuji, H. Poly(lactide) stereocomplexes: Formation, structure, properties, degradation, and applications. *Macromol. Biosci.* **5**, 569-597, (2005).
- 362 Tsuji, H. & Fukui, I. Enhanced thermal stability of poly(lactide)s in the melt by enantiomeric polymer blending. *Polymer* **44**, 2891-2896, (2003).
- 363 Li, W., Chen, X., Ma, Y. & Fan, Z. The accelerating effect of the star-shaped poly(d-lactide)-block-poly(l-lactide) stereoblock copolymer on PLLA melt crystallization. *CrystEngComm* **18**, 1242-1250, (2016).

- 364 Sarasua, J. R., Arraiza, A. L., Balerdi, P. & Maiza, I. Crystallinity and mechanical properties of optically pure polylactides and their blends. *Polym. Eng. Sci.* **45**, 745-753, (2005).
- 365 Tsuji, H. In vitro hydrolysis of blends from enantiomeric poly(lactide)s Part 1. Well-stereo-complexed blend and non-blended films. *Polymer* **41**, 3621-3630, (2000).
- 366 Li, Y. *et al.* Stereocomplex crystallite network in poly(d,l-lactide): formation, structure and the effect on shape memory behaviors and enzymatic hydrolysis of poly(d,l-lactide). *RSC Adv.* **5**, 24352-24362, (2015).
- 367 Li, Z., Tan, B. H., Lin, T. & He, C. Recent advances in stereocomplexation of enantiomeric PLA-based copolymers and applications. *Prog. Polym. Sci.* **62**, 22-72, (2016).
- 368 Tan, B. H., Muiruri, J. K., Li, Z. & He, C. Recent progress in using stereocomplexation for enhancement of thermal and mechanical property of polylactide. *ACS Sustainable Chem. Eng.* **4**, 5370-5391, (2016).
- 369 Soleymani Abyaneh, H., Vakili, M. R., Shafaati, A. & Lavasanifar, A. Block copolymer stereoregularity and its impact on polymeric micellar nanodrug delivery. *Mol. Pharm.* **14**, 2487-2502, (2017).
- 370 Brzeziński, M. & Biela, T. Micro- and nanostructures of polylactide stereocomplexes and their biomedical applications. *Polym. Int.* **64**, 1667-1675, (2015).
- 371 Ajiro, H., Kuroda, A., Kan, K. & Akashi, M. Stereocomplex film using triblock copolymers of polylactide and poly(ethylene glycol) retain paclitaxel on substrates by an aqueous inkjet system. *Langmuir* **31**, 10583-10589, (2015).
- 372 Ma, C. *et al.* Core-shell structure, biodegradation, and drug release behavior of poly(lactic acid)/poly(ethylene glycol) block copolymer micelles tuned by macromolecular stereostructure. *Langmuir* **31**, 1527-1536, (2015).
- 373 Agatemor, C. & Shaver, M. P. Tacticity-induced changes in the micellization and degradation properties of poly(lactic acid)-block-poly(ethylene glycol) copolymers. *Biomacromolecules* **14**, 699-708, (2013).
- 374 Yang, L., Wu, X., Liu, F., Duan, Y. & Li, S. Novel biodegradable polylactide/poly(ethylene glycol) micelles prepared by direct dissolution method for controlled delivery of anticancer drugs. *Pharm. Res.* **26**, 2332-2342, (2009).
- 375 Nederberg, F. *et al.* Simple approach to stabilized micelles employing miktoarm terpolymers and stereocomplexes with application in paclitaxel delivery. *Biomacromolecules* **10**, 1460-1468, (2009).
- 376 Fukushima, K. *et al.* Organocatalytic approach to amphiphilic comb-block copolymers capable of stereocomplexation and self-assembly. *Biomacromolecules* **9**, 3051-3056, (2008).
- 377 Chen, L., Xie, Z., Hu, J., Chen, X. & Jing, X. Enantiomeric PLA-PEG block copolymers and their stereocomplex micelles used as rifampin delivery. *Journal of Nanoparticle Research* **9**, 777-785, (2007).
- 378 Oh, J. K. Polylactide (PLA)-based amphiphilic block copolymers: synthesis, self-assembly, and biomedical applications. *Soft Matter* **7**, 5096-5108, (2011).
- 379 Zhao, Z. *et al.* Biodegradable stereocomplex micelles based on dextran-block-polylactide as efficient drug deliveries. *Langmuir* **29**, 13072-13080, (2013).
- 380 Ishii, D., Ying, T., Yamaoka, T. & Iwata, T. Characterization and biocompatibility of biopolyester nanofibers. *Materials* **2**, 1520, (2009).
- 381 Monticelli, O. *et al.* New stereocomplex PLA-based fibers: Effect of POSS on polymer functionalization and properties. *Macromolecules* **47**, 4718-4727, (2014).
- 382 Spasova, M. *et al.* Polylactide stereocomplex-based electrospun materials possessing surface with antibacterial and hemostatic properties. *Biomacromolecules* **11**, 151-159, (2010).
- 383 Fundador, N. G. V., Takemura, A. & Iwata, T. Structural properties and enzymatic degradation behavior of PLLA and stereocomplexed PLA nanofibers. *Macromol. Mater. Eng.* **295**, 865-871, (2010).

- 384 Zhang, X., Kotaki, M., Okubayashi, S. & Sukigara, S. Effect of electron beam irradiation on the structure and properties of electrospun PLLA and PLLA/PDLA blend nanofibers. *Acta Biomater.* **6**, 123-129, (2010).
- 385 Ishii, D. *et al.* In vivo tissue response and degradation behavior of PLLA and stereocomplexed PLA nanofibers. *Biomacromolecules* **10**, 237-242, (2009).
- 386 Tsuji, H. *et al.* Electrospinning of poly(lactic acid) stereocomplex nanofibers. *Biomacromolecules* **7**, 3316-3320, (2006).
- 387 Li, Y. *et al.* Broad-spectrum antimicrobial and biofilm-disrupting hydrogels: Stereocomplex-driven supramolecular assemblies. *Angew. Chem. Int. Ed.* **52**, 674-678, (2013).
- 388 Buwalda, S. J., Calucci, L., Forte, C., Dijkstra, P. J. & Feijen, J. Stereocomplexed 8-armed poly(ethylene glycol)-poly(lactide) star block copolymer hydrogels: Gelation mechanism, mechanical properties and degradation behavior. *Polymer* **53**, 2809-2817, (2012).
- 389 Abebe, D. G. & Fujiwara, T. Controlled thermoresponsive hydrogels by stereocomplexed PLA-PEG-PLA prepared via hybrid micelles of pre-mixed copolymers with different PEG lengths. *Biomacromolecules* **13**, 1828-1836, (2012).
- 390 Zhang, Y. *et al.* Novel thymopentin release systems prepared from bioresorbable PLA-PEG-PLA hydrogels. *Int. J. Pharm.* **386**, 15-22, (2010).
- 391 Nagahama, K., Fujiura, K., Enami, S., Ouchi, T. & Ohya, Y. Irreversible temperature-responsive formation of high-strength hydrogel from an enantiomeric mixture of starburst triblock copolymers consisting of 8-arm PEG and PLLA or PDLA. *J. Polym. Sci., Part A: Polym. Chem.* **46**, 6317-6332, (2008).
- 392 Jun, Y. J., Park, K. M., Joung, Y. K., Park, K. D. & Lee, S. J. In situ gel forming stereocomplex composed of four-arm PEG-PDLA and PEG-PLLA block copolymers. *Macromol. Res.* **16**, 704-710, (2008).
- 393 Hiemstra, C. *et al.* In vitro and in vivo protein delivery from in situ forming poly(ethylene glycol)-poly(lactide) hydrogels. *J. Controlled Release* **119**, 320-327, (2007).
- 394 Hiemstra, C., Zhong, Z., Li, L., Dijkstra, P. J. & Feijen, J. In-situ formation of biodegradable hydrogels by stereocomplexation of PEG-(PLLA)₈ and PEG-(PDLA)₈ star block copolymers. *Biomacromolecules* **7**, 2790-2795, (2006).
- 395 Fujiwara, T. *et al.* Novel thermo-responsive formation of a hydrogel by stereo-complexation between PLLA-PEG-PLLA and PDLA-PEG-PDLA block copolymers. *Macromol. Biosci.* **1**, 204-208, (2001).
- 396 Sun, L. *et al.* Structural reorganization of cylindrical nanoparticles triggered by polylactide stereocomplexation. *Nature Commun.* **5**, 5746, (2014).
- 397 Kim, S. H. *et al.* Hierarchical assembly of nanostructured organosilicate networks via stereocomplexation of block copolymers. *Nano Lett.* **8**, 294-301, (2008).
- 398 Wang, H. *et al.* Largely improved mechanical properties of a biodegradable polyurethane elastomer via polylactide stereocomplexation. *Polymer* **137**, 1-12, (2018).
- 399 Watts, A., Kurokawa, N. & Hillmyer, M. A. Strong, resilient, and sustainable aliphatic polyester thermoplastic elastomers. *Biomacromolecules* **18**, 1845-1854, (2017).
- 400 Huang, Y. *et al.* ABA-type thermoplastic elastomers composed of poly(ϵ -caprolactone-co- δ -valerolactone) soft midblock and polymorphic poly(lactic acid) hard end blocks. *ACS Sustainable Chem. Eng.* **4**, 121-128, (2016).
- 401 Wanamaker, C. L. *et al.* Consequences of polylactide stereochemistry on the properties of polylactide-polymenthide-polylactide thermoplastic elastomers. *Biomacromolecules* **10**, 2904-2911, (2009).
- 402 Zhang, Z., Grijpma, D. W. & Feijen, J. Triblock copolymers based on 1,3-trimethylene carbonate and lactide as biodegradable thermoplastic elastomers. *Macromol. Chem. Phys.* **205**, 867-875, (2004).
- 403 Marín, R. *et al.* Spectroscopic evidence for stereocomplex formation by enantiomeric polyamides derived from tartaric acid. *Macromolecules* **41**, 3734-3738, (2008).

- 404 Marín, R., Alla, A. & Muñoz-Guerra, S. Stereocomplex formation from enantiomeric
polyamides derived from tartaric acid. *Macromol. Rapid Commun.* **27**, 1955-1961, (2006).
- 405 Iribarren, I. *et al.* Stereocopolyamides derived from 2,3-di-*O*-methyl-D- and -L-tartaric acids
and hexamethylenediamine. 2. Influence of the configurational composition on the crystal
structure of optically compensated systems. *Macromolecules* **29**, 8413-8424, (1996).
- 406 Nakano, K., Hashimoto, S., Nakamura, M., Kamada, T. & Nozaki, K. Stereocomplex of
poly(propylene carbonate): Synthesis of stereogradient poly(propylene carbonate) by regio-
and enantioselective copolymerization of propylene oxide with carbon dioxide. *Angew.
Chem. Int. Ed.* **50**, 4868-4871, (2011).
- 407 Auriemma, F., De Rosa, C., Di Caprio, M. R., Di Girolamo, R. & Coates, G. W. Crystallization of
alternating limonene oxide/carbon dioxide copolymers: Determination of the crystal
structure of stereocomplex poly(limonene carbonate). *Macromolecules* **48**, 2534-2550,
(2015).
- 408 Auriemma, F. *et al.* Stereocomplexed poly(limonene carbonate): A unique example of the
cocrystallization of amorphous enantiomeric polymers. *Angew. Chem. Int. Ed.* **54**, 1215-
1218, (2014).
- 409 Zhu, J.-B. & Chen, E. Y. X. Catalyst-sidearm-induced stereoselectivity switching in
polymerization of a racemic lactone for stereocomplexed crystalline polymer with a circular
life cycle. *Angew. Chem. Int. Ed.* **58**, 1178-1182, (2019).
- 410 Zhu, J.-B., Watson, E. M., Tang, J. & Chen, E. Y. X. A synthetic polymer system with
repeatable chemical recyclability. *Science* **360**, 398, (2018).
- 411 Jing, Y., Quan, C., Liu, B., Jiang, Q. & Zhang, C. A mini review on the functional biomaterials
based on poly(lactic acid) stereocomplex. *Polym. Rev.* **56**, 262-286, (2016).
- 412 Tsuji, H., Noda, S., Kimura, T., Sobue, T. & Arakawa, Y. Configurational molecular glue: One
optically active polymer attracts two oppositely configured optically active polymers. *Sci.
Rep.* **7**, 45170, (2017).
- 413 Tsuji, H. & Hayakawa, T. Heterostereocomplex- and homocrystallization and thermal
properties and degradation of substituted poly(lactic acid)s, poly(l-2-hydroxybutanoic acid)
and poly(d-2-hydroxy-3-methylbutanoic acid). *Macromol. Chem. Phys.* **217**, 2483-2493,
(2016).
- 414 Tsuji, H. & Hayakawa, T. Hetero-stereocomplex formation between substituted poly(lactic
acid)s with linear and branched side chains, poly(l-2-hydroxybutanoic acid) and poly(d-2-
hydroxy-3-methylbutanoic acid). *Polymer* **55**, 721-726, (2014).
- 415 Tsuji, H., Yamamoto, S., Okumura, A. & Sugiura, Y. Heterostereocomplexation between
biodegradable and optically active polyesters as a versatile preparation method for
biodegradable materials. *Biomacromolecules* **11**, 252-258, (2010).
- 416 Schuster, N. J. *et al.* A helicene nanoribbon with greatly amplified chirality. *J. Am. Chem. Soc.*
140, 6235-6239, (2018).
- 417 Khokhlov, K., Schuster, N. J., Ng, F. & Nuckolls, C. Functionalized helical building blocks for
nanoelectronics. *Org. Lett.* **20**, 1991-1994, (2018).
- 418 Zhong, Y. *et al.* Helical nanoribbons for ultra-narrowband photodetectors. *J. Am. Chem. Soc.*
139, 5644-5647, (2017).
- 419 Zhang, B. *et al.* Hollow organic capsules assemble into cellular semiconductors. *Nature
Commun.* **9**, 1957, (2018).
- 420 Zhang, B. *et al.* Rigid, conjugated macrocycles for high performance organic photodetectors.
J. Am. Chem. Soc. **138**, 16426-16431, (2016).
- 421 Ball, M. *et al.* Macrocyclization in the design of organic n-type electronic materials. *J. Am.
Chem. Soc.* **138**, 12861-12867, (2016).
- 422 Ball, M. *et al.* Chiral conjugated corrals. *J. Am. Chem. Soc.* **137**, 9982-9987, (2015).
- 423 Shin, S. *et al.* Living light-induced crystallization-driven self-assembly for rapid preparation of
semiconducting nanofibers. *J. Am. Chem. Soc.* **140**, 6088-6094, (2018).

- 424 Li, S., Han, G. & Zhang, W. Concise synthesis of photoresponsive polyureas containing
bridged azobenzenes as visible-light-driven actuators and reversible photopatterning.
Macromolecules **51**, 4290-4297, (2018).
- 425 Zhou, H. *et al.* Photoswitching of glass transition temperatures of azobenzene-containing
polymers induces reversible solid-to-liquid transitions. *Nature Chem.* **9**, 145, (2016).
- 426 Accardo, J. V. & Kalow, J. A. Reversibly tuning hydrogel stiffness through photocontrolled
dynamic covalent crosslinks. *Chem. Sci.*, (2018).
- 427 Roppolo, I. *et al.* 3D printable light-responsive polymers. *Mater. Horizons* **4**, 396-401, (2017).
- 428 Nehls, E. M., Rosales, A. M. & Anseth, K. S. Enhanced user-control of small molecule drug
release from a poly(ethylene glycol) hydrogel via azobenzene/cyclodextrin complex tethers.
J. Mater. Chem. B, **4**, 1035-1039, (2016).
- 429 Rosales, A. M., Mabry, K. M., Nehls, E. M. & Anseth, K. S. Photoresponsive elastic properties
of azobenzene-containing poly(ethylene-glycol)-based hydrogels. *Biomacromolecules* **16**,
798-806, (2015).
- 430 Tamesue, S., Takashima, Y., Yamaguchi, H., Shinkai, S. & Harada, A. Photoswitchable
supramolecular hydrogels formed by cyclodextrins and azobenzene polymers. *Angew. Chem.*
Int. Ed. **49**, 7461-7464, (2010).
- 431 Zhao, Y.-L. & Stoddart, J. F. Azobenzene-based light-responsive hydrogel system. *Langmuir*
25, 8442-8446, (2009).
- 432 Donovan, B. R., Matavulj, V. M., Ahn, S.-k., Guin, T. & White, T. J. All-optical control of shape.
Adv. Mater. **31**, 1805750, (2019).
- 433 Hassan, F., Sassa, T., Hirose, T., Ito, Y. & Kawamoto, M. Light-driven molecular switching of
atropisomeric polymers containing azo-binaphthyl groups in their side chains. *Polym. J.* **50**,
455-465, (2018).
- 434 Yang, D. *et al.* Fabrication of chiroptically switchable films via co-gelation of a small chiral
gelator with an achiral azobenzene-containing polymer. *Soft Matter* **13**, 6129-6136, (2017).
- 435 Yang, D., Duan, P., Zhang, L. & Liu, M. Chirality and energy transfer amplified circularly
polarized luminescence in composite nanohelix. *Nature Commun.* **8**, 15727, (2017).
- 436 Cobos, K., Quiñoá, E., Riguera, R. & Freire, F. Chiral-to-chiral communication in polymers: A
unique approach to control both helical sense and chirality at the periphery. *J. Am. Chem.*
Soc. **140**, 12239-12246, (2018).