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Application of the $S_{2\infty}$ and C_∞ point groups for the prediction of polymer chirality

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Polymer chirality assignment is achieved with the first chemical applications of the $S_{2\infty}$ and C_∞ molecular point groups to infinite cyclic polymers, obviating the usual dependence on translational symmetry operations.

The classification of a molecule as chiral or achiral depends essentially on the point group of that molecule. Any molecule belonging to the point groups C_1, C_n, D_n, T, O, or I is chiral; otherwise it is achiral.[1] This assignment is often straightforward for small molecules but cannot be applied generally to synthetic polymers because a typical polymeric sample contains a multitude of unique, structurally distinct species. Therefore, chirality prediction in linear macromolecules has relied on three chain models:[2] a finite chain model with identical end groups;[3] a finite chain model with different end groups;[4] and an infinite chain model.[5] Each of these models has been gainfully applied. However, since none rely on molecular point group assignment, it seemed advantageous to devise a universal model that could reliably predict a polymer's chiroptical properties based on the straightforward point group rule for chirality stated above.

In 1965, Natta *et al.* reported the conversion of the infinite chain model to a finite cyclic model that applied symmetry elements to four- and six-membered rings.[6,7] This is an acceptable construct for identifying many chiral polymers, but tactic polymers with main-chain directionality were not fully addressed. Herein such polymers are considered with an *infinite* cyclic model, resulting in the first chemical applications of the $S_{2\infty}$ and C_∞ molecular point groups.[8]

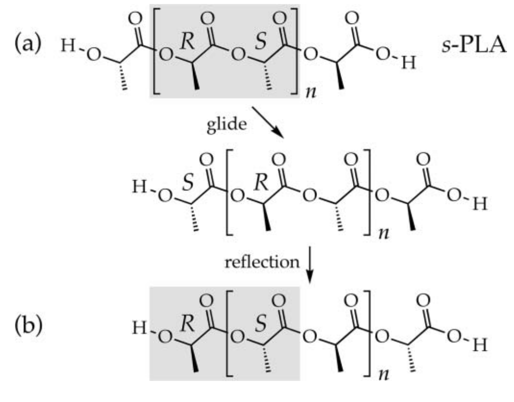

Fig. 1 Syndiotactic poly(lactic acid) (a) is considered achiral because of the glide–reflection symmetry operation that generates the original rendition of the repeat unit (b).

Syndiotactic poly(lactic acid) (*s*-PLA, Fig. 1a) is a tactic polymer of recent origin with main-chain directionality.[9] A randomly selected polymer chain has C_1 symmetry—yet the bulk material does not exhibit optical activity. This observation is readily explained upon identification of a glide–reflection symmetry operation that yields the original representation of the repeat unit (Fig. 1b). The presence of this reflective symmetry mandates achirality—at least in the limit of large n.

Now consider (presently unknown) *cyclic s*-PLA with n repeat units (Fig. 2). The glide–reflection symmetry operation is now equivalent to the rotation–reflection, which is the S_{2n} improper rotation. In the artificial limit of infinite n—which serves best to assess the chiroptical properties of the corresponding high molecular weight linear polymer—this molecule bears the $S_{2\infty}$ improper axis, but no mirror planes of symmetry and thus, should be assigned to the $S_{2\infty}$ point group. Note that an improper axis generates the set of operations S_n, S_n^2, S_n^3, …, but the result is different for even and odd n.[10] The present case pertains to even order improper axes because, as concluded from Fig. 2, the S_{2n} symmetry operation is applicable and $2n$ must be even for integral

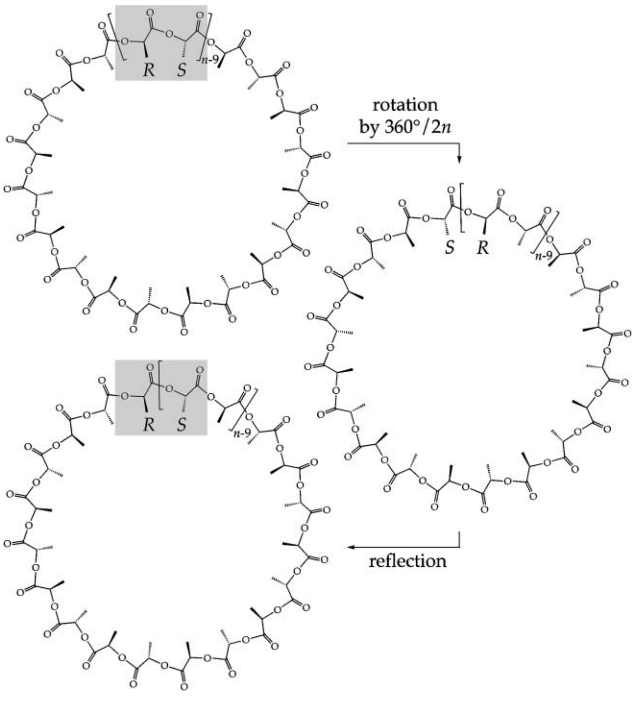

Fig. 2 Cyclic *s*-PLA is a member of the S_{2n} point group and thus is achiral. The depicted rotation–reflection constitutes the S_{2n} symmetry operation. As n approaches infinity, the $S_{2\infty}$ point group applies.

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values of n. Therefore, it is more rigorous to describe the present point group as $S_{2\infty}$ (instead of S_∞) since this designation more clearly implies even order axes.

The group multiplication table for the point group $S_{2\infty}$ is presented in Table 1. Note that $S_{2\infty}{}^{2\infty} = E$ and that the symmetry operations $S_{2\infty}{}^{\text{even}}$ reduce to $C_{2\infty}{}^{\text{even}}$.[10] Also—as might be guessed from the alternating presence of i and C_2 in the S_2 ($=C_i$), S_4, S_6, S_8, S_{10}, and S_{12} point groups—$S_{2\infty}{}^{\infty}$ is equivalent to i for $\infty = 2n + 1$, but equivalent to C_2 for $\infty = 2n$. The collection of symmetry operations is infinite, but can be denoted as

$$E,\ S_{2\infty},\ S_{2\infty}{}^3,\ S_{2\infty}{}^5,\ \ldots,\ S_{2\infty}{}^{2\infty-1},\ C_{2\infty}{}^2,\ C_{2\infty}{}^4,\ C_{2\infty}{}^6,\ \ldots,\ C_{2\infty}{}^{2\infty-2},\ i$$

or

$$E,\ S_{2\infty},\ S_{2\infty}{}^3,\ S_{2\infty}{}^5,\ \ldots,\ S_{2\infty}{}^{2\infty-1},\ C_{2\infty}{}^2,\ C_{2\infty}{}^4,\ C_{2\infty}{}^6,\ \ldots,\ C_{2\infty}{}^{2\infty-2},\ C_2$$

depending on whether ∞ is considered odd or even, respectively. Each set constitutes a novel mathematical, Abelian group. In the former case, these symmetry operations correspond to those of the well-known $D_{\infty h}$ point group upon desymmetrization *via* elimination of all σ_v and C_2 ($\perp$ to the principal axis) symmetry operations.

Isotactic poly(lactic acid) (*i*-PLA),[11–13] another tactic polymer with main-chain directionality, can be considered analogously. The only symmetry elements present for the cyclic polymer with n repeat units are the proper axes of rotation C_n, $C_n{}^2$, $C_n{}^3$, … (Fig. 3). Accordingly, the infinite cyclic polymer is a member of the C_∞ point group, mandating assignment of the original linear polymer as chiral. The C_∞ group multiplication table (Table 2) is readily obtained from that of $S_{2\infty}$ upon exclusion of all improper rotations. One may note that desymmetrization of the well-known $C_{\infty v}$ point group by removal of the σ_v symmetry operations yields C_∞.

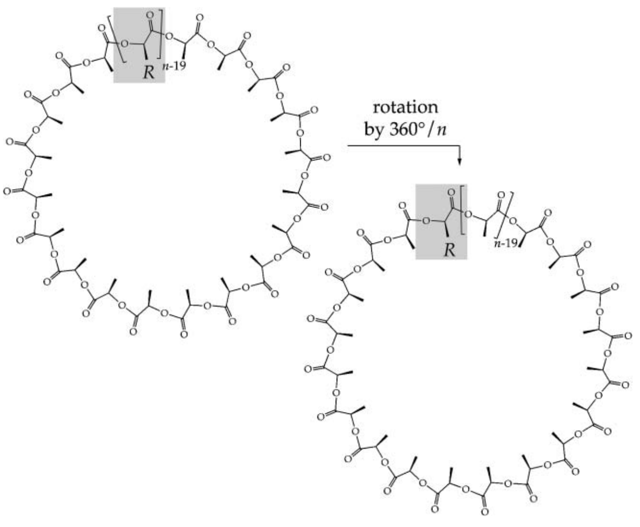

Fig. 3 Cyclic *i*-PLA is a member of the C_n point group and thus is chiral. The depicted rotation constitutes the C_n symmetry operation. As n approaches infinity, the C_∞ point group applies.

Table 2 Group multiplication table for the molecular point group C_∞

C_∞	E	C_∞	$C_\infty{}^2$	…	$C_\infty{}^{\infty-2}$	$C_\infty{}^{\infty-1}$
E	E	C_∞	$C_\infty{}^2$	…	$C_\infty{}^{\infty-2}$	$C_\infty{}^{\infty-1}$
C_∞	C_∞	$C_\infty{}^2$	$C_\infty{}^3$	…	$C_\infty{}^{\infty-1}$	E
$C_\infty{}^2$	$C_\infty{}^2$	$C_\infty{}^3$	$C_\infty{}^4$	…	E	C_∞
…	…	…	…	…	…	…
$C_\infty{}^{\infty-2}$	$C_\infty{}^{\infty-2}$	$C_\infty{}^{\infty-1}$	E	…	$C_\infty{}^{\infty-4}$	$C_\infty{}^{\infty-3}$
$C_\infty{}^{\infty-1}$	$C_\infty{}^{\infty-1}$	E	C_∞	…	$C_\infty{}^{\infty-3}$	$C_\infty{}^{\infty-2}$

In summary, the development of a universal point group formalism for the prediction of polymer chirality has identified the first chemical applications of the $S_{2\infty}$ and C_∞ molecular point groups. Linear tactic polymers with main-chain directionality are converted to an infinite cyclic model and considered as members of these point groups. Assignment as achiral ($S_{2\infty}$) or chiral (C_∞) then proceeds without any dependence on translational symmetry operations, such as glide–reflection. Group multiplication tables

Table 1 Group multiplication table for the molecular point group $S_{2\infty}$[a]

$S_{2\infty}$	E	$S_{2\infty}$	$C_{2\infty}{}^2$	$S_{2\infty}{}^3$	$C_{2\infty}{}^4$	…	$S_{2\infty}{}^\infty$	…	$C_{2\infty}{}^{2\infty-4}$	$S_{2\infty}{}^{2\infty-3}$	$C_{2\infty}{}^{2\infty-2}$	$S_{2\infty}{}^{2\infty-1}$
E	E	$S_{2\infty}$	$C_{2\infty}{}^2$	$S_{2\infty}{}^3$	$C_{2\infty}{}^4$	…	$S_{2\infty}{}^\infty$	…	$C_{2\infty}{}^{2\infty-4}$	$S_{2\infty}{}^{2\infty-3}$	$C_{2\infty}{}^{2\infty-2}$	$S_{2\infty}{}^{2\infty-1}$
$S_{2\infty}$	$S_{2\infty}$	$C_{2\infty}{}^2$	$S_{2\infty}{}^3$	$C_{2\infty}{}^4$	$S_{2\infty}{}^5$	…	$S_{2\infty}{}^{\infty+1}$	…	$S_{2\infty}{}^{2\infty-3}$	$C_{2\infty}{}^{2\infty-2}$	$S_{2\infty}{}^{2\infty-1}$	E
$C_{2\infty}{}^2$	$C_{2\infty}{}^2$	$S_{2\infty}{}^3$	$C_{2\infty}{}^4$	$S_{2\infty}{}^5$	$C_{2\infty}{}^6$	…	$S_{2\infty}{}^{\infty+2}$	…	$C_{2\infty}{}^{2\infty-2}$	$S_{2\infty}{}^{2\infty-1}$	E	$S_{2\infty}$
$S_{2\infty}{}^3$	$S_{2\infty}{}^3$	$C_{2\infty}{}^4$	$S_{2\infty}{}^5$	$C_{2\infty}{}^6$	$S_{2\infty}{}^7$	…	$S_{2\infty}{}^{\infty+3}$	…	$S_{2\infty}{}^{2\infty-1}$	E	$S_{2\infty}$	$C_{2\infty}{}^2$
$C_{2\infty}{}^4$	$C_{2\infty}{}^4$	$S_{2\infty}{}^5$	$C_{2\infty}{}^6$	$S_{2\infty}{}^7$	$C_{2\infty}{}^8$	…	$S_{2\infty}{}^{\infty+4}$	…	E	$S_{2\infty}$	$C_{2\infty}{}^2$	$S_{2\infty}{}^3$
…	…	…	…	…	…	…	…	…	…	…	…	…
$S_{2\infty}{}^\infty$	$S_{2\infty}{}^\infty$	$S_{2\infty}{}^{\infty+1}$	$S_{2\infty}{}^{\infty+2}$	$S_{2\infty}{}^{\infty+3}$	$S_{2\infty}{}^{\infty+4}$	…	E	…	$S_{2\infty}{}^{\infty-4}$	$S_{2\infty}{}^{\infty-3}$	$S_{2\infty}{}^{\infty-2}$	$S_{2\infty}{}^{\infty-1}$
…	…	…	…	…	…	…	…	…	…	…	…	…
$C_{2\infty}{}^{2\infty-4}$	$C_{2\infty}{}^{2\infty-4}$	$S_{2\infty}{}^{2\infty-3}$	$C_{2\infty}{}^{2\infty-2}$	$S_{2\infty}{}^{2\infty-1}$	E	…	$S_{2\infty}{}^{\infty-4}$	…	$C_{2\infty}{}^{2\infty-8}$	$S_{2\infty}{}^{2\infty-7}$	$C_{2\infty}{}^{2\infty-6}$	$S_{2\infty}{}^{2\infty-5}$
$S_{2\infty}{}^{2\infty-3}$	$S_{2\infty}{}^{2\infty-3}$	$C_{2\infty}{}^{2\infty-2}$	$S_{2\infty}{}^{2\infty-1}$	E	$S_{2\infty}$	…	$S_{2\infty}{}^{\infty-3}$	…	$S_{2\infty}{}^{2\infty-7}$	$C_{2\infty}{}^{2\infty-6}$	$S_{2\infty}{}^{2\infty-5}$	$C_{2\infty}{}^{2\infty-4}$
$C_{2\infty}{}^{2\infty-2}$	$C_{2\infty}{}^{2\infty-2}$	$S_{2\infty}{}^{2\infty-1}$	E	$S_{2\infty}$	$C_{2\infty}{}^2$	…	$S_{2\infty}{}^{\infty-2}$	…	$C_{2\infty}{}^{2\infty-6}$	$S_{2\infty}{}^{2\infty-5}$	$C_{2\infty}{}^{2\infty-4}$	$S_{2\infty}{}^{2\infty-3}$
$S_{2\infty}{}^{2\infty-1}$	$S_{2\infty}{}^{2\infty-1}$	E	$S_{2\infty}$	$C_{2\infty}{}^2$	$S_{2\infty}{}^3$	…	$S_{2\infty}{}^{\infty-1}$	…	$S_{2\infty}{}^{2\infty-5}$	$C_{2\infty}{}^{2\infty-4}$	$S_{2\infty}{}^{2\infty-3}$	$C_{2\infty}{}^{2\infty-2}$

[a] The symmetry operation $S_{2\infty}{}^\infty$ is equivalent to i for $\infty = 2n + 1$, but equivalent to C_2 for $\infty = 2n$. $S_{2\infty}{}^{\text{even}}$ reduce to $C_{2\infty}{}^{\text{even}}$.

for these infinite Abelian groups are presented and derivation of their character tables will be presented elsewhere.

Importantly, the universal point group formalism is of considerable pedagogical benefit for efficiently characterizing the chiroptical properties of macromolecules, which would not be amenable to strict point group classification without the unusual $S_{2\infty}$ and C_∞ molecular point groups presented. While these point groups only apply to molecules of infinite and imaginary structure, they nonetheless highlight valuable chemical applications of group theory.

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