Good practice report

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Chirality analysis of helical polymers

Abstract: Optically active macromolecules, having a preferred- or single-handed helical conformation, play important roles in polymeric materials and in life. This article presents how helical polymers can be assessed from a view of chirality. These assessments, based on optical rotation (OR) and circular dichroism (CD) spectral measurements with associated information, include theoretical spectral calculations as well as chromatographic resolution. Specific applied examples are discussed for poly(9,9-dioctylfluorene-2,7-diyl) and derivatives, stereoregular polyolefins bearing centers of chirality in the side chain, isotactic poly(triphenylmethyl methacrylate), and π-stacked poly(dibenzofulvene). For more convincing establishment of a helix, it is important to correlate chiroptical properties with related information such as molar-mass effects, temperature effects, and chemical transformation effects on the properties. Helices of the polyolefins and poly(TrMA) were confirmed considering these aspects. In addition, comparison of chiroptical properties between the polymer in question and a monomeric unit model compound generally helps to confirm a helix. There are no general, reliable methods to quantify helical sense excess. On the other hand, absolute helical sense can be determined by comparing experimental and theoretical CD spectra as well as considering exciton coupling effects in CD spectra. The former method can be more generally applied for a wide range of polymers as far as a good model for calculations is designed, while the latter can be more conveniently and empirically applied for a certain class of polymer structures that are suited to exhibit exciton coupling without using computers.

Keywords: chromatographic resolution; circular dichroism spectra; exciton coupling; helix; optical rotation; polymer; theoretical calculations.

Introduction

Asymmetric structures of macromolecules play important roles in polymeric materials and in life. Their chiral structures are based mainly on two elements of chirality, i.e., central chirality and helical chirality (axial chirality). If centers of chirality or helical chains comprise of an excess amount of either enantiomeric structure (one of the mirror images), the polymer may show optical properties including optical rotation (OR) and circular dichroism (CD) ("chiroptical properties"). One can thus obtain information on polymer chirality by measuring such properties. The experiments for chirality analysis of polymers do not differ from those of small molecules; however, results may need to be carefully interpreted when OR and CD spectral data are used to establish chiral polymer structure.

This article introduces analytical methods of chirality including OR and CD spectroscopy used for polymers, as well as how results can be interpreted in order to understand polymer chirality that is focused on the helical conformation of synthetic polymers with preferred or single handedness. Optically active helical polymers find a wide variety of applications, including resolution of racemic compounds, asymmetric

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catalysis, and non-linear optics, with some of them having been successfully commercialized (Okamoto & Nakano, 2000; Okamoto, Matsuda, Nakano, & Yashima, 1994; Yashima et al., 2016). While helical polymers are popular subjects of research work in polymer science, helical conformation needs to be confirmed and evaluated carefully on the basis of OR and CD spectra with additional, associated information.

Chirality analysis is generally taught at undergraduate level, focusing on basic theories in addition to hands-on measurement training using typical, chiral small molecules. At graduate level, knowledge may be deepened to encompass properties of polarized light as well as basic structures of a polarimeter and CD spectrometer. On the other hand, the topic of polymer chirality analysis is often not covered, even in graduate school, possibly due to the fact that the identification of helical polymers is not as straightforward as that of chiral small molecules. This article focuses on the very aspects that are seemingly complicated in analyzing helical polymers. Through learning helical polymer analyses, students are given clues how they can gain information about rather complex, chemical systems, not limited to helical polymers. In addition, this article provides brief information on theoretical analysis. Becoming aware of the usefulness of computer calculations through helical polymer analyses, students will learn to expand their scopes in a variety of aspects of chemistry, not just chirality, even if they are not specialized in computer science, with the aid of existing software and affordable personal computers that are widely available in the modern research environment.

Optical rotation (OR)

Optical rotation (OR) measurements using a polarimeter determine the rotation angle (α) of the plane of polarization of linearly polarized light (LPL) about the optical axis that travels through a chiral material. Rotation occurs on the basis of a difference in reflective index of left- and right-handed circularly polarized light (CPL) that form the components of LPL; the two CPLs travel at different rates through a chiral material. A general polarimeter is comprised of a light source, a linear polarizer creating incident LPL, and another, rotatable linear polarizer for detection aligned in this order (Figure 1). The chiral sample is inserted between the first and second linear polarizers. The light source is often a Hg or Na lamp, leading to values at certain, discrete wavelengths.

In order to obtain information of molecular chirality by avoiding the effects of sample anisotropy, the sample should be a homogeneous, isotropic fluid. As polymers are generally solid materials, an isotropic solution is made as the sample, which is then put into an optical cell. Consequently, caution must be made during sample preparation and interpretation of the resulting data because incomplete dissolution can lead to inaccurate sample concentration. Moreover, any undissolved polymer may scatter the incident light beam, which would result in inaccurate rotation values.

The rotation angle, α, is normalized into specific rotation ($[\alpha]$) according to the following equation:

$$[\alpha]_\lambda^T = 100 \times \alpha/lc$$

where α is the rotation angle (°), T is the temperature, λ is the wavelength of the light used, l is the cell path length (dm), and c is the sample concentration (g/dL).
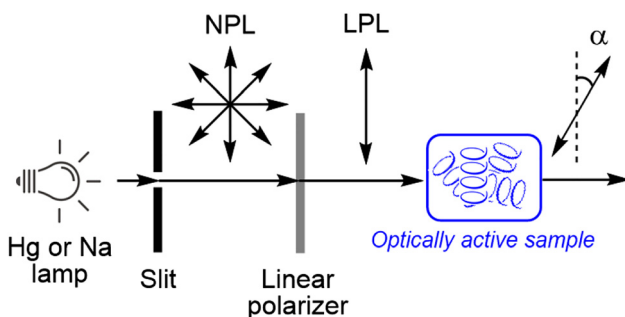

Figure 1: Schematic diagram of a polarimeter.

Optical rotatory dispersion (ORD) is the spectrum version of OR, where the relationship between OR and the wavelength is presented as a continuous curve. This, however, has been reported for rather limited cases.

Circular dichroism (CD)

A circular dichroism (CD) spectrum is a differential absorption spectrum of left- and right-handed CPLs. A chiral material may have different absorbance coefficients toward left- and right-handed CPLs and may show CD. Because either L- or R-CPL is absorbed more strongly by the sample, the light passed through the sample is, in general, elliptically polarized light (EPT). A general CD spectrometer is comprised of a Xe light source, a monochromator, a linear polarizer, a photo elastic modulator (PEM) that creates L- and R-CPL, and a photo-detector (often a photomultiplier tube, PMT) aligned in this order where the chiral sample is inserted in between the PEM and PMT (Figure 2).

A homogeneous, isotropic solution of polymer leads to a CD spectrum with the highest precision. The presence of undissolved polymer particles leads to inaccurate concentration and may scatter the incident light beam, resulting in inaccurate spectra.

The spectrometer gives an elliptical angle, or ellipticity (θ), which is defined as the tangent of the ratio of the minor to major elliptical axes of the EPT as primary information about the chiral sample. Similarly to optical rotation, ellipticity is normalized into molar ellipticity ($[\theta]$) according to the following equation:

$$[\theta] = \theta \times M/lc\,(\text{cm}^2\text{dmol}^{-1})$$

where θ is the ellipticity (°), M is the molar mass, l is the cell path length (dm), and c is the sample concentration (g/dL).

CD intensity is also expressed in delta absorbance ($\Delta\varepsilon$) which is the difference in molar absorptivity between L- and R-CPL. $\Delta\varepsilon$ and $[\theta]$ are correlated with each other by the following equation:

$$[\theta] = 3298.2 \times \Delta\epsilon\,(\text{dm}^3\text{mol}^{-1}\text{cm}^{-1})$$

A continuous plot of $[\theta]$, or $\Delta\varepsilon$, against wavelength is a CD spectrum. A CD spectrum and ORD are theoretically interchangeable by the Kramers–Kronig relations (Kramers, 1927; Kronig, 1926; Shapiro et al., 1995).

An important point in practical CD spectral measurements is to keep the concentration of sample within the range where the PMT can linearly respond. If a sample has too high a concentration, and light going through the sample is too weak (dark), the PMT may generate false signals where even achiral benzene could appear CD active.

Establishing and evaluating helical structure

Helix or not

Chiroptical properties of a polymer may be based on a center of chirality and/or an axis of chirality (helix) and/or a plane of chirality with unequal populations of right- and left-handed enantiomeric structures.
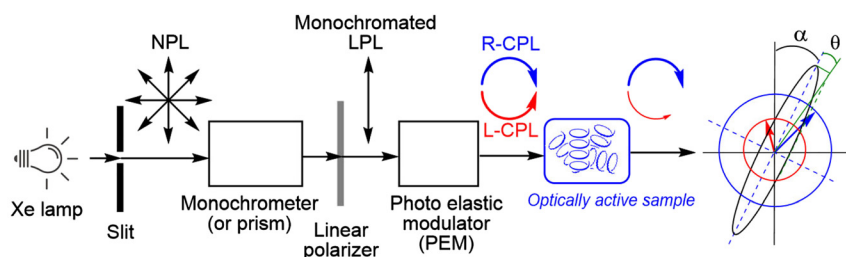

Figure 2: Schematic diagram of a CD spectrometer.

If a polymer has no centers or planes of chirality, the observed chiroptical properties are reasonably ascribed to conformational chirality. While any conformation having no planes of symmetry can account for chiroptical properties, a helix may be proposed as the simplest one. As a typical example of a helical polymer having no centers or planes of chirality, optically active poly(9,9-dioctylfluorene-2,7-diyl) has been reported (Figure 3A) (Pietropaolo, Wang, & Nakano, 2015; Wang, Sakamoto, & Nakano, 2012; Wang, Harada, Phuong, Kanemitsu, & Nakano, 2018). Because axial chirality around the single bond's connecting monomeric units is the only chiral element for this polymer, a preferred-handed twist is reasonably proposed to explain its chiroptical properties, and accumulated twists of the same hand in a chain means a preferred-handed helix. A helix can be thus deduced based only on chiroptical properties and simple, non-computational structural consideration for such a simple polymer. For this particular example, more accurate conclusions were obtained by theoretical calculations, as discussed later.

If a polymer has centers of chirality, and, at the same time, they may have helical conformation, the helix needs to be established carefully. Considering (a) molar-mass effects, (b) temperature effects, (c) chemical transformation effects, and (d) chiroptical properties of the monomeric unit, model compounds may be important in confirming helix. When chiroptical properties do not remarkably change by these effects, they may arise mainly from centers of chirality because these effects can significantly affect the helix.

For example, the helix of stereoregular polyolefins bearing centers of chirality in the side chain was established considering molar-mass effects and temperature effects (Pino & Lorenzi, 1960). OR values of the polymers were higher for higher-molar-mass fractions (molar mass effects), and the OR of helical polymers changed to a greater extent than for small-molecular model compounds (temperature effects). The logic is that OR values based purely on centers of chirality in the side chain would not significantly change depending on molar-mass or temperature while OR values based on a helix could be because a longer chain would stabilize the helix and because the conformation may change depending on temperature. In addition, OR values of the polymers were much greater than those of the monomeric unit model compounds.
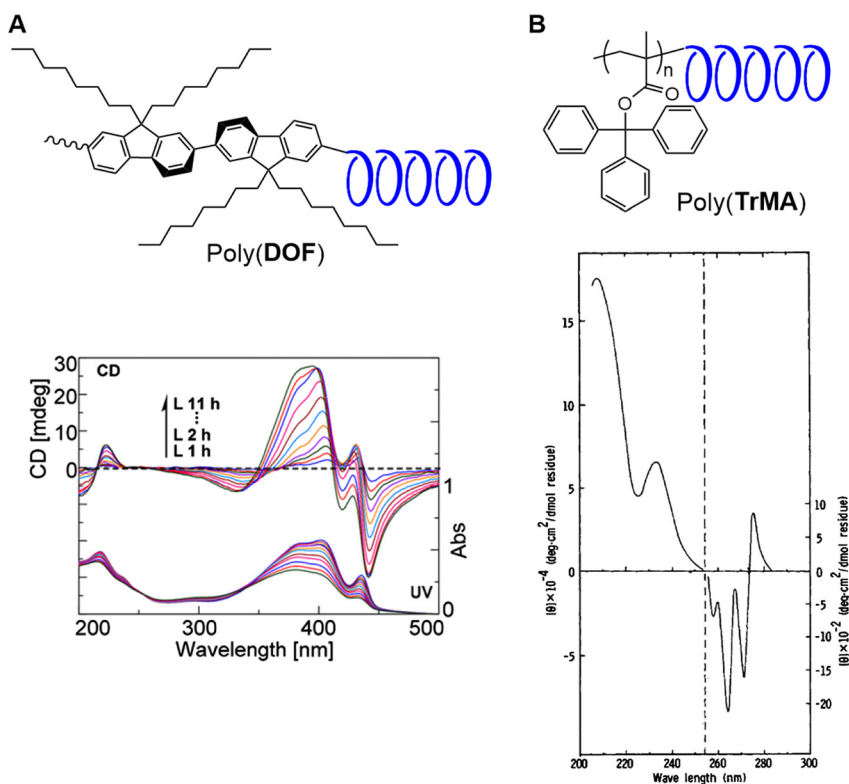
Figure 3: Structures (top) and CD spectra (bottom) of typical helical polymers: poly(DOF) (A) and poly(TrMA) (B) [reproduced from references Wang et al. (2012) (A) and Okamoto et al. (1979) (B) with permissions].

As another example, the helix of poly(triphenylmenthyl methacrylate) (poly[TrMA]), the first example of single-handed helical vinyl polymer having no centers of chirality in the side chain, was supported by molar-mass effects and chemical transformation effects (Figure 3B) (Nakano, Okamoto, & Hatada, 1992; Okamoto, Suzuki, Ohta, Hatada, & Yuki, 1979; Okamoto, Suzuki, & Yuki, 1980; Okamoto, Okamoto, & Yuki, 1981). Helical conformation of this polymer was proposed based on its almost entirely isotactic main-chain configuration, implying two aspects of stereochemistry; first, an isotactic chain has a plane of symmetry (mirror plane) orthogonal to it, and second, an isotactic chain can be reasonably folded into a helical shape, which may result in remarkable OR and CD spectra. Further, the remarkable chiroptical properties were only observed for higher-molar-mass chains and not for oligomers up to 8-mer (molar-mass effects). In addition, the proposed helical conformation was considered to be maintained by the steric repulsion between bulky triphenymethyl groups in the side chain. This was evidenced by solvolysis of the side chain leading to poly(methacrylic acid) and, following methylation, to poly(methyl methacrylate) (poly[MMA]) with a random conformation, showing only negligible OR (chemical transformation effects).

Helical-sense excess (h.e.)

As chromatographic chiral resolution of racemates is widely applicable for small molecules, determination of enantiomeric excess (e.e.) can be unambiguously conducted through such experiments. Chiral small molecules may be derived from natural compounds having 100% e.e. through reliable synthetic routes having no racemization. Relationships between e.e. and OR and CD spectra of many small molecules have been published, and e.e. of a sample can be determined based on observed chiroptical properties through comparison with literature information about specimens. In sharp contrast, resolution of a polymer helix can be extremely difficult and has not been attained except for very limited examples. This is why specimens of single-handed helical polymers are virtually unavailable so far, and h.e. has not been reported for most synthetic, helical polymers.

A renowned exception is poly(TrMA), whose single-handed helix (h.e. ~100%) was established by a very careful open column chromatographic resolution using optically active poly(TrMA) itself as a chiral stationary phase (Figure 4) (Okamoto et al., 1981). A poly(TrMA) sample, which was a mixture of right- and left-handed helices, was resolved on (+)-poly(TrMA) into a number of fractions, among which, the first-eluted was (−)-poly(TrMA) showing the greatest absolute value of OR. This sample was again resolved under the same conditions, resulting in fractions showing almost the same OR as the (−)-poly(TrMA) obtained through the first resolution. These results indicate that the (−)-poly(TrMA) sample did not contain any (+)-fraction, which means that it had a single-handed helical conformation. This example is truly exceptional, and such a careful analysis has not been reported for most other helical polymers.

Determination of h.e. is therefore not possible for most helical polymers. Nevertheless, a single-handed helix is often concluded for new polymers simply because "large" OR or CD spectral intensity is observed. Because the intensity cannot be discussed without a specimen, "preferred-handed helix" is generally a more appropriate expression.

Absolute helical sense, left or right

X-ray analysis of single crystals can afford information of the absolute configuration of small molecules. This is the most general way of the determination of absolute configuration. Polymers, however, do not form single crystals mainly due to variation in chain lengths contained in the sample, leaving the left-handed or right-handed helix question still open for most helical polymers.

When CD spectra show clear Cotton splitting (a bisignate curve), considerations of exciton coupling effects may lead to absolute helical sense information (Figure 5) (Harada, Nakanishi, & Berova, 2012). Exciton
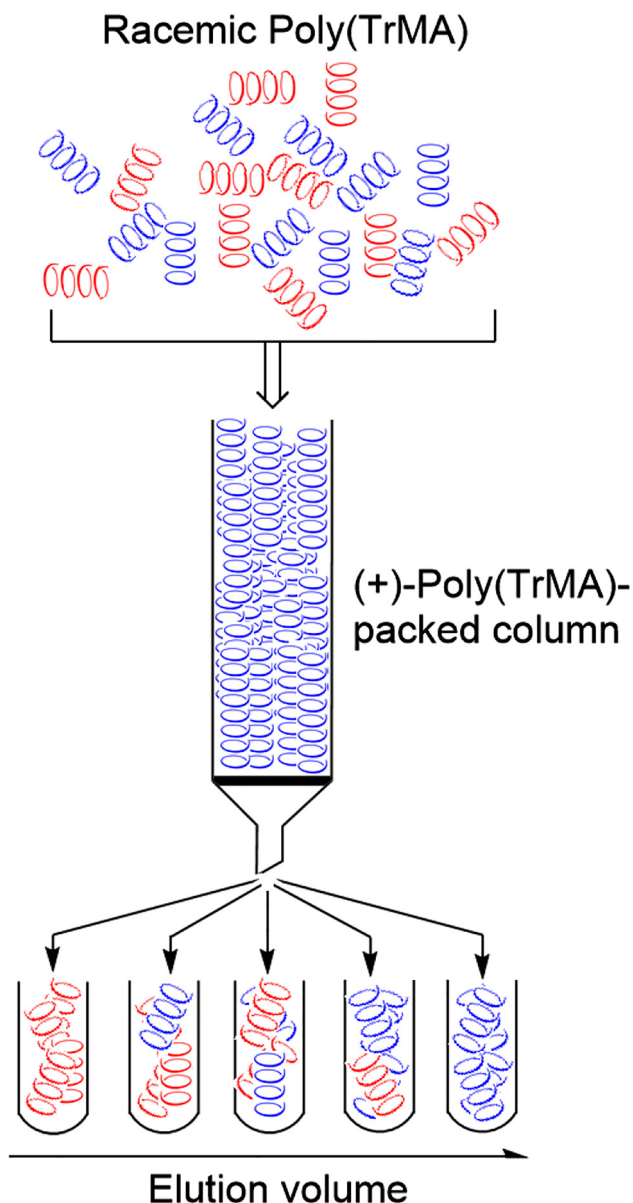
Figure 4: Resolution of left- and right-handed helices of poly(TrMA) leading to a single-handed helical sample.

coupling can occur between two or more identical, or very similar, chromophores located close enough in a molecule or a polymer in a twisted, chiral arrangement. If the dihedral angle related to the chromophore's arrangement has a positive sign, positive Cotton splitting may be observed. Although this method itself has a solid theoretical background, it is often prone to errors due to insufficient structural information and spectral complexity with overlapping bands.

Computational methods

Chiroptical properties can be rationally interpreted based upon helical conformation including absolute helical sense using (theoretical) computational chemistry methods. Molecular simulations can predict most plausible conformations and their OR and CD spectra. The simulations can also accurately deduce signs of OR and CD for optimized structures if suitable conditions are chosen (Nakano, Tanikawa, Nakagawa, Yade, &
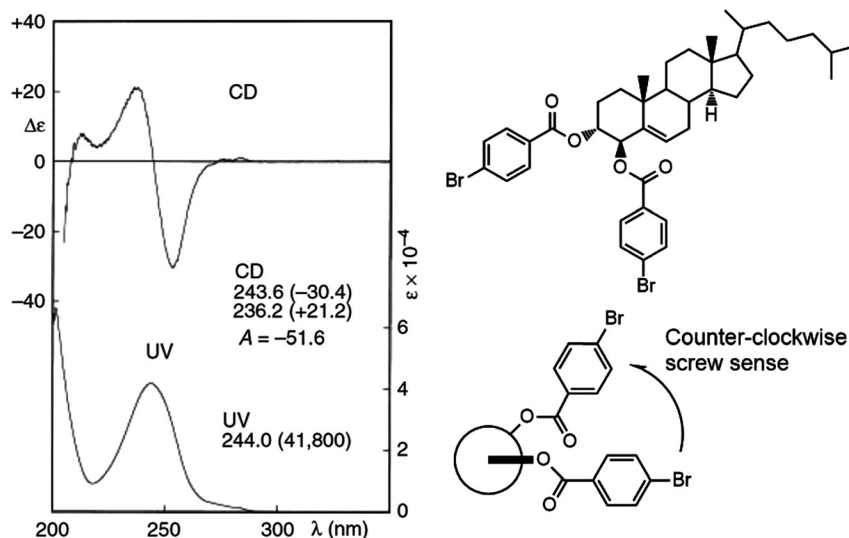
Figure 5: CD/UV spectra and structures of cholest-5-ene-3β,4β-diol bis(p-bromobenzoate) showing negative exciton chirality [redrawn from reference Okamoto et al. (1979) with permission].

Sakamoto, 2009; Pietropaolo & Nakano, 2013, 2020; Pietropaolo, Cozza, Zhang, & Nakano, 2018; Sakamoto, Fukuda, Sato, & Nakano, 2009). In the case of poly(9,9-dioctylfluroene-2,7-diyl) discussed earlier, the presence and the absolute helical sense of the helix were concluded by the following: (1) the most probable conformation was estimated, (2) theoretical CD spectra were calculated for the conformation, and (3) matching of the theoretical CD spectra with experimental CD spectra was confirmed (Figure 6) (Pietropaolo et al., 2015). The combination of experiments and theoretical calculations is thus a powerful method of chirality analysis of the helix. Other examples of helical conformational analyses combining experimental data and theoretical calculations include studies of polyacrylate (Pietropaolo & Nakano, 2013; Sakamoto et al., 2009) and poly(dibenzofulvene) (Nakano & Yade, 2003; Nakano, Takewaki, Yade, & Okamoto, 2001; Nakano et al., 2004; Pietropaolo et al., 2018).

However, it should be noted that real polymer systems are generally too large for calculations within a reasonable time. Proposing good, smaller models is therefore crucial in obtaining reliable results. In addition, calculation of accurate values of OR and CD intensity is still challenging, meaning that theoretical methods need to be improved to determine h.e.

GUI-based software packages are available, and some of them can run on Windows and Mac OS. The most representative software may be Gaussian (Frisch et al., 2016) or open-source ab-initio software such as OpenMolcas (Fdez. Galván et al., 2019), and QuantumEspresso (Giannozzi et al., 2009) featuring various types of calculation methods. Popular molecular dynamics software, such as GROMACS (Hess, Kutzner, van der Spoel, & Lindahl, 2008), NAMD (Phillips et al., 2005), LAMMPS (Plimpton, 1995), and open-source libraries like PLUMED (Bonomi et al., 2019), can be used to predict structural and molecular dynamical properties. Open source visualization packages, VMD (Humphrey, Dalke, & Schulten, 1996) and Avogadro (Hanwell et al., 2012), among others, can be useful to visualize and analyze the conformations of simulated molecules.

Other chiroptical spectroscopies

Vibrational CD (VCD) spectroscopy leads to chirality information on vibrational transitions; it is the IR version of CD spectroscopy. As most compounds are IR-active, VCD can give chirality information of a wide range of polymers including those containing no UV-active chromophores, such as polysaccharides, while overall sensitivity of measurements tends to be lower for VCD than CD. In addition, Raman optical activity (ROA) measurements can afford chirality information of polymers having no chromophores, while availability of ROA apparatus is not yet high at present.

A

B
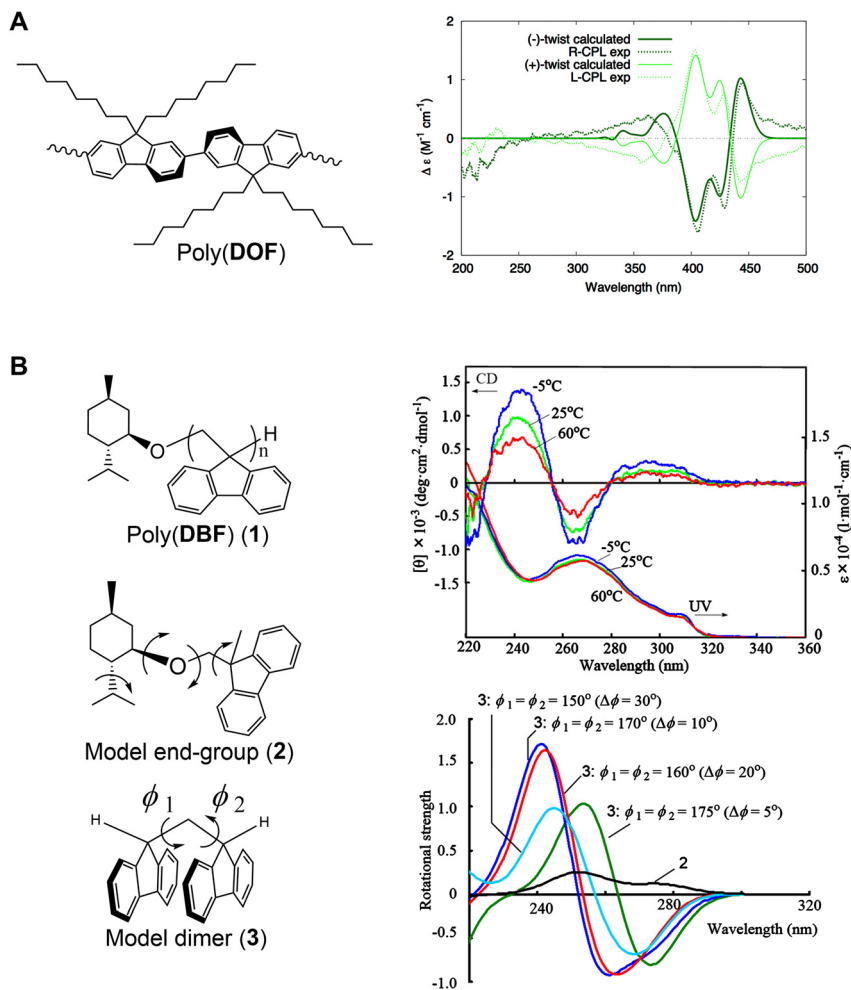
Figure 6: Structures (left) and CD spectra (right) of helical polymers: (A) poly(DOF) and (B) poly(DBF) (**1**) with a model unimer (**2**) and dimer (**3**) [reproduced from references Pietropaolo et al. (2015) (A) and Nakano et al. (2009) (B) with permissions].

Conclusions

Methods of chiroptical property measurements were overviewed in connection with structural analysis of helical polymers. Although OR and CD spectra lead to principal information on the chirality of polymers, chiroptical information alone is not sufficient to characterize helical conformation. Three typical examples of helical polymers were discussed, namely poly(9,9-dioctylfluorene-2,7-diyl) and derivatives, stereoregular polyolefins bearing centers of chirality in the side chain, and isotactic poly(TrMA). In the simplest case, a helix can be proposed based only on chiroptical properties and simple, non-computational structural consider-ations, which was the case for poly(9,9-dioctylfluorene-2,7-diyl) and derivatives. For more convincing establishment of a helix, it is important to correlate observed chiroptical properties with associating infor-mation. Molar-mass effects, temperature effects, and chemical transformation effects on chiroptical properties should be considered because a helix may be generally more stable for a higher-molar-mass polymer; the helical shape or sense may change depending on temperature and chemical structural changes may damage helical conformation. Helices of polyolefins and poly(TrMA) were confirmed considering these aspects. In addition, comparison of chiroptical properties between the polymer in question and a monomeric unit model compound helps to confirm a helix.

On the other hand, there have not been any general, reliable methods to quantify h.e. and to determine the absolute helical sense just through experiments. Although helical sense in some cases may be guessed on the basis of exciton coupling effects, such a method is prone to errors and should be used carefully.

   Theoretical calculations giving rise to optimized conformations and corresponding chiroptical spectral data can result in reliable information for helix characterization. The combination of experiments and theoretical calculations is a powerful method of chirality analysis of a helix. However, it should be noted that spectral intensity calculations leading to h.e. determination are still challenging and that reliable calculations may be obtained only when appropriate conditions are chosen and a good model structure for computation is proposed.

Supplementary information

A set of protocols for the analysis of molecular simulations are available at the following PLUMED tutorial page https://www.plumed.org/doc-v2.4/user-doc/html/cineca.html.

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