Helical polymers

Otto Vogl
Polytechnic University, 333 Jay Street, Brooklyn, New York 11201, USA

and Gary D. Jaycox
Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, USA
(Received 2 February 1987; revised 11 May 1987; accepted 3 June 1987)

A number of natural and synthetic helical polymers are briefly described. The relationship between polymer helicity and optical activity is discussed. The synthesis of optically active polymers based solely on macromolecular asymmetry is emphasized.

(Keywords: polymer conformation; helix; macromolecular asymmetry; optical activity)

Macromolecules exist in a variety of conformational forms. These range from randomly coiled chains to more spatially ordered structures. Of particular interest are those polymers which adopt helical symmetry, either in solution or in the solid state. Helical geometry is a consequence of an orderly repetition of internal rotational angles along the polymer backbone and is commonly encountered among polymers of both natural and synthetic origin.

As detailed by Cahn, Ingold and Prelog[1], a helix is characterized by a central axis (*c*-axis), a screw sense and a pitch. For a helical polymer, pitch P, or the distance travelled along the *c*-axis corresponding to one full 360° turn, is related to n, the number of monomer units in each turn, and h, the monomer repeat height projected onto the *c*-axis, where $P = n \times h$. Helix symmetry is designated by N_m, where N residues reside in m turns of the helical screw. The symbols (+) and (−) further denote a right- or left-handed screw sense, respectively.

The most extensively studied class of macromolecules possessing helical order are the proteins and their synthetic analogues, the poly(α-amino acids). The α-helix, a right-handed 18_5 helical structure with 3.6–3.7 residues per turn has long been recognized as an integral part of many proteins. First identified from X-ray diffraction studies by Pauling in 1951[2], the α-helix exists both in the solid state and in solution. The helix derives considerable stabilization from internal hydrogen bonding between –NH– and carbonyl groups positioned at regular intervals along the helical coil. For α-helices composed of the naturally occurring *l*-amino acids, a right-handed screw sense is energetically favoured over the left-handed form, although a few exceptions are known[3]. Other conformational arrangements of the poly(α-amino acid) backbone have also been experimentally observed. These include an anti-parallel β-sheet (technically a degenerate 2_1 helix), the 3_1 helix of polyglycine II, a left-handed 3_1 helix observed for polyproline II and the ω-helix common to a number of synthetic polypeptides[4].

Helical order is also encountered among the nucleic acids. The double helical geometry of deoxyribonucleic acid (DNA) is particularly well known. A number of DNA polymorphs have been identified in the solid state depending upon the experimental conditions used to obtain fibres for X-ray diffraction studies. The B-conformation of DNA, thought to most closely approximate the native state of the macromolecule, is formed in the presence of NaCl or LiCl under conditions of high relative humidity. In this structure, two sugar–phosphate chains, situated in anti-parallel fashion, are wound about a common, central axis into a right-handed helical screw (diameter 20 Å). The two strands are joined by hydrogen bonds between complementary base pairs which occupy the internal regions of the helix. As first deduced by Watson and Crick[5,6] in 1953, B-DNA is characterized by ten-fold symmetry, with each perpendicular base pair rising some 3.4 Å along the helix axis. In contrast, C-DNA formed under slightly different conditions, possesses 28_3 helical symmetry with 9.33 nucleotides per turn and a nucleotide repeat of 3.3 Å against the helix axis[7,8]. A-DNA, a right-handed 11_1 arrangement with a 2.6 Å nucleotide repeat has also been experimentally observed[8]. A radically different left-handed double-helical structure has been encountered for certain synthetic polynucleotides. Z-DNA, with its left-handed, zig-zag appearance is characterized by twelve-fold symmetry and a dinucleotide repeat of 7.43 Å[9]. Despite its ladder-like structure, DNA is not a rigid macromolecule but rather possesses considerable macroscopic flexibility both in solution and in its native environment.

Helicity is also common to the third class of biopolymers, the polysaccharides. α-Amylose, a major component of starch, forms helical structures in solution, with 6 to 7 glucose units per turn[10]. This helix is stabilized by hydrogen bonds which bridge the polymer's hydroxyl groups. The helical cavity of α-amylose is large enough to easily accommodate a number of guest species, including water, iodine, benzene and a variety of aliphatic compounds[11]. Other solid state helical structures have also been identified[12,13].

The helical order encountered among the biopolymers is largely stabilized by the presence of hydrogen bonds, hydrophobic–hydrophilic interactions and ionic attractions between charged groups along the polymer chains. These secondary bonding forces allow many native

0032-3861/87/132179–04$03.00

macromolecules to maintain their helical geometry in aqueous environments. Only when subjected to strong acids or alkali, detergents or higher temperatures do these molecules unfold or denature to a random coil state. Helix to random coil transitions in biopolymers are of considerable theoretical and experimental interest[14].

In contrast to their native cousins, most synthetically derived macromolecules lack the secondary bonding forces which stabilize helical order in solution. For these polymers, helicity is generally reserved for the solid state where crystalline packing forces dictate conformational geometry. Because extended helices can be easily incorporated into a regular crystalline lattice, a helical arrangement of the polymer backbone is highly favoured in the solid state. Indeed, the helix is the most common systematic, ordered structure encountered among the synthetic, crystalline polymers[14]. A number of examples are described below.

Linear polyethylene, the simplest carbon–hydrogen containing polymer, crystallizes in a planar zig-zag arrangement where each unit comprises a full turn in a degenerate helix[14,15]. The polymers of formaldehyde, $-(CH_2-O)_n-$, and thioformaldehyde, $-(CH_2-S)_n-$, are characterized by 2_1 helical order, with monomer repeats along the *c*-axis (helix axis) of 1.8 and 2.2 Å, respectively[16,17].

Crystallographic studies have shown that isotactic vinyl polymers of the form $-(CH_2-CHX)_n-$ also possess solid state helical order. Helix symmetry is governed by the relative size of X, ranging from 3_1 helices for polypropylene, polystyrene and poly(vinyl methyl ether)[18–20] to the larger 7_2 and 4_1 arrangements observed for poly(1-hexene) and poly(vinyl cyclohexane), respectively[21,22]. Helix pitch, the product of *n* and *h*, ranges from 6.5 to 7.0 Å for polymers in this category.

The isotactic polyaldehydes are characterized by four-fold helical symmetry in the solid state. With monomer repeats along the *c*-axis of 1.2 to 1.3 Å (due to a short carbon–oxygen bond length of 1.41 Å), polyaldehyde helices are generally wound wider and tighter than their vinyl counterparts, with a pitch of only 4.8 to 5.2 Å[23,24].

Also crystallizing in helical form are the polymers of the ethylene oxides[25,26]. Poly(ethylene oxide) itself is locked into a 7_2 helical arrangement with a monomer repeat of about 2.8 Å. In sharp contrast to the crystalline polyaldehydes, these carbon–oxygen containing polymers are relatively low melting and are quite soluble even in hydrocarbon media.

Other significant macromolecular helical structures include the 2_1 helices of the polyesters[27–29] the 2_1 screws of nylon-6 and nylon-12[30,31], syndiotactic polypropylene with 4_1 helical order[32] and the 10_1 double helix of isotactic poly(methyl methacrylate)[33].

The structural properties of a number of helical macromolecules have been compiled in *Table 1*. Included for each polymer are helix symmetry (approximate), helix pitch, monomer repeat distance, and other relevant information.

The chiroptical properties of the helical polymers deserve special mention. As the data in *Table 1* indicate, poly(α-amino acid) and nucleic acid helices are characterized by a unique screw direction. One helical

Table 1 Characteristic properties of some helical polymers

Polymer poly-	Helix symmetry	Helix pitch[a] (*c*-axis) (Å)	Monomer repeat (*c*-axis) (Å)	Backbone atoms in monomer unit	T_m[b] (°C)
Formaldehyde	2_1	3.6	1.8	2	178
Thioformaldehyde	2_1	4.3	2.2	2	260 dec.
Acetaldehyde*	4_1	4.8	1.2	2	165 dec.
n-Butyraldehyde*	4_1	4.8	1.2	2	225 dec.
Isobutyraldehyde*	4_1	5.2	1.3	2	>260 dec.
Trichloroacetaldehyde	4_1	5.2	1.3	2	dec.
Propylene*	3_1	6.6	2.2	2	170
Butene-1*	3_1	6.6	2.2	2	132–142[c]
Styrene*	3_1	6.6	2.2	2	245
Vinyl methyl ether*	3_1	6.6	2.2	2	144
Hexene-1*	7_2	7.0	2.0	2	-55
4-Methyl pentene-1*	7_2	7.0	2.0	2	230
Vinyl cyclohexane*	4_1	6.5	1.6	2	300, 383*
3-Methylbutene-1*	4_1	6.8	1.7	2	306
Methyl methacrylate*	10_1 (Double-helix)	21	2.1	2	>200
Ethylene oxide	7_2	9.8	2.8	3	70
Isopropyl ethylene oxide*	2_1	5.6	2.8	3	52
Pivalolactone	2_1	6.0	3.0	4	240
α-Amino acids					
α helix	18_5	(+) 5.5	1.5	3	35–45 denatured
poly-*l*-proline II	3_1	(−) 9.4	3.1	3	
polyglycine II	3_1	9.3	3.1	3	
ω-helix	4_1	(−) 5.3	1.3	3	
Nucleic acids					
B-DNA	10_1	(+)33.8	3.38	6	≃85 denatured
A-DNA	11_1	(+)28.1	2.56	6	
C-DNA	28_3	(+)30.9	3.31	6	
Z-DNA	12_1	(−)44.6	7.43 (dinucleotide)	6	

* Isotactic

[a] (+) for right-hand, (−) for left-hand helices

[b] T_m values approximate

[c] Depending on crystalline form or initiator used for preparation

coil, right or left, is energetically favoured over the other by the presence of chiral centres which reside within the α-amino acid or nucleotide residues of these macromolecules. Here, optical activity is a consequence of asymmetry, i.e. chirality, at both the atomic and macromolecular levels.

A particularly interesting development in recent years has been the synthesis of optically active helical polymers in which *all* activity arises from macromolecular asymmetry, i.e. a preferred or exclusive helical screw sense. Because polymers of this type lack main chain or side chain asymmetric carbon atoms, right and left helical screws are energetically equivalent, and therefore, equally probable during the course of polymerization with simple initiators. However, a predominance of one helical screw direction can be obtained in one of two ways: (1) through a complete or partial resolution of a helical screw pair with the aid of a chiral substrate, or (2) through the use of chiral initiating species which preferentially induce the formation of one helical screw sense over the other. Presently, a limited number of optically active helical polymers have been prepared via these two routes. These include the polymers of trichloroacetaldehyde (chloral), triphenylmethyl methacrylate and the isocyanides.

In the solid state, isotactic polychloral is locked into a tight 4_1 helical screw with a 1.3 Å monomer repeat[34–36]. The polymer is insoluble in all conventional organic solvents. With the aid of chiral initiators, Vogl and coworkers[37–45] have prepared polychloral having a preferred helical direction. Specific rotations of up to 5000° (sodium D-line) have been measured in solid films[42]. A similar approach has been used by Yuki and Hatada for optically active poly(triphenylmethyl methacrylate) with specific rotations reaching 400° (sodium D-line) in solution[46,47]. In contrast, Drenth and coworkers employed a chiral support to partially resolve the right- and left-handed 4_1 helical coils of their optically inactive, i.e. racemic poly(tert-butyl isocyanide). This procedure gave an optically active polymer with a specific rotation of −16° at the sodium D-line[48,49].

The preparation of optically active polymers based solely on macromolecular asymmetry requires that the polymer chain form a tight helix which is incapable of undergoing conformational inversion. Moreover, if chiral initiators are used to induce a preferred screw sense, the initiation and propagation steps which lead to the formation of the helix must occur with a high degree of stereoselectivity[50,51]. Although much of the initial work in this field has been done with isotactic polymers, this is not a necessary requirement. Ultimately, helical polymers like poly(tetrafluoroethylene) and poly(tetramethyl ethylene oxide) should be capable of displaying macromolecular asymmetry.

Other helical macromolecules having unique chiroptical properties include quartz[52], an inorganic polymer, a family of helicene oligomers with optical rotations in excess of 9000°[10], and cholesteric liquid crystals which form macroscopic helical assemblies[53,54].

CONCLUSION

In summary, helical order is encountered among a wide variety of macromolecules and is often responsible for the physical and biological properties of these systems. The origin and maintenance of helicity is a consequence of both the physical characteristics of the polymer, i.e. tacticity, nature of side groups and the particular environment into which it is placed. The chiroptical properties of helical macromolecules are particularly interesting. Helical polymers with optical activity arising entirely from macromolecular asymmetry are a relatively new development and represent an exciting area for future study.

ACKNOWLEDGEMENTS

This work was supported in part by a grant from the PPG Corporation, Pittsburg, PA, USA, and the Herman F. Mark Chair of the Polytechnic University, Brooklyn, NY, USA. We appreciate the many valuable and encouraging suggestions and comments from J. H. Richards at the California Institute of Technology, Pasadena, CA, USA. The assistance of E. Cary and L. L. Barrow in the preparation of this manuscript is gratefully acknowledged.

REFERENCES

1 Cahn, R. S., Ingold, C. and Prelog, V. *Angew. Chem., Int. Edn. Engl.* 1966, **5**, 385

2 Pauling, L. and Corey, R. B. *Proc. Natl. Acad. Sci. USA* 1951, **37**, 235

3 Karlson, R. H., Norland, K. S., Fasman, G. D. and Blout, E. R. *J. Am. Chem. Soc.* 1960, **82**, 2268

4 Walton, A. G. 'Polypeptides and Protein Structure', Elsevier North Holland, Inc., New York, 1981, pp. 17–49

5 Watson, J. D. and Crick, F. H. C. *Nature* 1953, **171**, 737

6 Watson, J. D. and Crick, F. H. C. *Nature* 1953, **171**, 967

7 Marvin, D. A., Spencer, M., Wilkins, M. H. F. and Hamilton, L. D. *J. Mol. Biol.* 1961, **3**, 547

8 Fuller, W., Wilkins, M. H. F., Wilson, H. R. and Hamilton, L. D. *J. Mol. Biol.* 1965, **12**, 601

9 Wang, A. H.-J., Quigley, G. J., Kolpak, F. J., van der Marel, G., van Boom, J. H. and Rich, A. *Science* 1980, **211**, 171

10 Meurer, K. P. and Vogtle, F. 'Helical Molecules in Organic Chemistry', in 'Topics in Current Chemistry', Vol. 127, (Ed. F. L. Boschke), Springer-Verlag, New York, 1985, pp. 32–41

11 Hui, Y., Russell, J. C. and Whitten, D. G. *J. Am. Chem. Soc.* 1983, **105**, 1374

12 Rundle, R. E. and French, D. *J. Am. Chem. Soc.* 1943, **65**, 1707

13 Sarko, A. and Marchessault, R. H. *J. Am. Chem. Soc.* 1967, **89**, 6454

14 Poland, D. and Scheraga, H. A. 'Theory of Helix-Coil Transitions in Biopolymers', Academic Press, New York, 1970

15 Tadokoro, H. 'Structure of Crystalline Polymers', John Wiley and Sons, Inc., New York, 1979

16 Uchida, T. and Tadokoro, H. *J. Polym. Sci. A*-2 1967, **5**, 63

17 Carazzolo, G. and Valle, G. *Makromol. Chem.* 1966, **90**, 66

18 Natta, G. and Corradini, P. *Nuovo Cimento, Suppl.* 1960, **15**, 40

19 Natta, G. and Corradini, P. *Makromol. Chem.* 1955, **16**, 77

20 Corradini, P. and Bassi, I. W. *J. Polym. Sci. C* 1968, **16**, 3233

21 Turner-Jones, A. *Makromol. Chem.* 1964, **71**, 1

22 Natta, G., Corradini, P. and Bassi, I. W. *Makromol. Chem.* 1959, **33**, 247

23 Natta, G., Mazzanti, G., Corradini, P. and Bassi, I. W. *Makromol. Chem.* 1960, **37**, 156

24 Natta, G., Corradini, P. and Bassi, I. W. *J. Polym. Sci.* 1961, **51**, 505

25 Takahashi, Y. and Tadokoro, H. *Macromolecules* 1973, **6**, 672

26 Takahashi, Y., Tadokoro, H., Hirano, T., Sato, A. and Tsurua, T. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 285

27 Yokouchi, M., Chatani, Y., Tadokoro, H., Teranishi, K. and Tani, H. *Polymer* 1973, **14**, 267

28 Yokouchi, M., Chatani, Y., Tadokoro, H. and Tani, H. *Polym. J.* 1974, **6**, 248

29 Carazzolo, G. *Chim. Ind.* (*Milan*) 1964, **46**, 525

30 Arimoto, H., *J. Polym. Sci. A* 1964, **2**, 2283

31 Inoue, K. and Hoshino, S. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 1077

32 Corradini, P., Natta, G., Ganis, P. and Temussi, P. A. *J. Polym. Sci. C* 1967, **16**, 2477

33 Kusanagi, H., Tadokoro, H. and Chatani, Y. *Macromolecules* 1976, **9**, 531

34 Kubisa, P., Corley, L. S., Kondo, T., Jacovic, M. and Vogl, O. *Polym. Eng. Sci.* 1981, **21**, 829

35 Brame, E. G., Raevsky, A. M., Semin, G. K., Jaycox, G. D. and Vogl, O. *Polym. Bull.* 1983, **10**, 521

36 Wasai, G., Iwata, T., Hirono, K., Kuragano, M., Saegusa, T. and Furukawa, F. *Kogyo Kagaku Zasshi* 1964, **67**, 1920

37 Corely, L. S. *Ph.D. Dissertation*, University of Massachusetts, Amherst (1979)

38 Corley, L. S. and Vogl, O. *Polym. Bull.* 1980, **3**, 211

39 Harris, W. J. *Ph.D. Dissertation*, University of Massachusetts, Amherst (1982)

40 Harris, W. J. and Vogl, O. *Polym. Prepr., ACS Div. Polym. Chem.* 1981, **22**(2), 309

41 Hatada, K., Shimizu, S., Yuki, H., Harris, W. J. and Vogl, O. *Polym. Bull.* 1981, **4**, 179. Corrections 1981, **4**, 683

42 Jaycox, G. D. *M.S. Thesis*, University of Massachusetts, Amherst (1984)

43 Zhang, J., Jaycox, G. D. and Vogl. O. *Polym. Prepr., ACS Div. Polym. Chem.* 1985, **26**(1), 156

44 Vogl, O. *The Chemist* 1985, **62**(9), 16

45 Vogl, O. and Jaycox, G. D. *Chemtech.* 1986, **16**, 698

46 Okamoto, Y., Suzuki, K., Ohta, K., Hatada, K. and Yuki, H. *J. Am. Chem. Soc.* 1979, **101**, 4763

47 Okamoto, Y., Suzuki, K. and Yuki, H. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 3043

48 Nolte, R. J. M., van Beijnen, A. J. M. and Drenth, W. *J. Am. Chem. Soc.* 1974, **96**, 5932

49 Drenth, W. and Nolte, R. J. M. *Acc. Chem. Res.* 1979, **12**, 30

50 Abe, A., Tasaki, K., Inomata, K. and Vogl, O. *Macromolecules* 1986, **19**, 2707

51 Zhang, J., Jaycox, G. D. and Vogl, O. *Polym. J.* (*Jpn.*), in press

52 Biot, J. B. *Mem. Inst.* 1912, **1**, 1

53 Friedel, G. *Ann. Phys.* 1922, **18**, 273

54 Mason, S. F. 'Molecular Optical Activity and the Chiral Discriminations', Cambridge University Press, Cambridge, England, 1982, pp. 97–100