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New Thermotropic Chiral Nematic Copolymers. 2.[†] A Study of Helical Sense and Twisting Power Based on Copolymers Containing (*S*)-(−)-1-Phenylethanol and (*R*)-(−)-Methyl Mandelate

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ABSTRACT: New thermotropic chiral nematic copolymers containing (*S*)-(−)-1-phenylethanol and (*R*)-(−)-methyl mandelate plus previously reported copolymers containing (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine and (−)-5-cholesten-3β-ol (i.e., cholesterol) combine to serve as the basis for the investigations of helical sense and twisting power. It was found that, instead of optical rotation or absolute configuration, chiral/nematic molecular interactions of a steric nature dictate the configurational characteristics that are responsible for the twist sense. Furthermore, an increased chiral/nematic structural similarity appears to contribute to an enhanced helical twisting power (HTP); a bulkier chiral moiety does not necessarily give rise to a higher HTP value.

I. Introduction

One of the approaches to the preparation of thermotropic liquid crystals exhibiting the cholesteric mesophase is to dope a nematic host with a chiral compound.[1] The helical sense, as defined by the sense of the reflected circularly polarized light,[2,3] and twisting power are the two key issues that are not only intriguing from a fundamental standpoint but also critical to practical applications in the fabrication of a variety of optical devices.[4] In principle, the predictions of helical sense and twisting power could be accomplished on the basis of both the nematic/nematic and chiral/nematic molecular interactions. In fact, the molecular theory formulated by Goossens[5] was successfully employed to interpret several chiral/nematic system parameters including helical twisting power, temperature dependence of the pitch, and the effect of the nematic host on the pitch.[6] Moreover, molecular models incorporating both steric (i.e., short-range) and hydrogen-bonding (i.e., long-range) interactions have met with considerable success in furnishing physical insights into the origin of helical sense.[7-11] Nevertheless, a priori predictions of helical sense and twisting power are complicated by the delicate and intricate nature of molecular interactions; the utility of the molecular statistical approach was found to be limited to structurally simple systems.[12]

From a technological perspective, thermotropic polymers comprising both nematogenic and chiral comonomers are preferred over low molar mass counterparts in view of the environmental robustness attributable to the potential glassy state of polymeric materials. Such a multifunctional methodology based on the spacer concept[13] is the theme of our investigations of helical sense and twisting power in relation to macromolecular structure. In two recent papers,[14,15] we have demonstrated that the enantiomers as part of the pendant group give rise to opposite helical sense in the resultant chiral nematic copolymers. In the present study, an attempt is made to interpret helical sense based on the configurational characteristics of the chiral moiety using new chiral nematic copolymers containing (*S*)-(−)-1-phenylethanol and (*R*)-(−)-methyl mandelate in addition to the previously reported[14,15] (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine and (−)-5-cholesten-3β-ol (i.e., cholesterol). The helical twisting power of these chiral compounds will also be compared to each other in the macromolecular structural settings that permit a thorough investigation of the effects of structural parameters.

II. Experimental Section

All the reagents necessary for the synthesis of monomers and copolymers were the same as used previously[14,15] with the exception of (*S*)-(−)-1-phenylethanol (98+%, American Tokyo Kasei) and (*R*)-(−)-methyl mandelate (99+%, Aldrich Chemical Co.). The experimental procedures and the instrumentation for characterization were all as described elsewhere[14,15] except that the optical elements were consistently annealed at 95% of the clearing temperature prior to the measurement of λ_R, the selective reflection wavelength.

III. Results and Discussion

The chemical structures of the monomers and chiral nematic copolymers synthesized and characterized for the present study are given in Table I and II, respectively. Table III presents the structural, thermal, and optical characterization results for the new copolymers. Copolymers containing (*S*)-(−)-1-phenylethylamine[14] and cholesterol[15] are also included in Table II for comparative purposes. Copolymers 1, 2 (based on (*S*)-(−)-1-phenylethylamine), and 3 are all found to give left-handed helical structures at the supramolecular level although the absolute configuration, defined by the Cahn–Ingold–Prelog rule,[16] of (*R*)-(−)-methyl mandelate is opposite to that of (*S*)-(−)-1-phenylethylamine or (*S*)-(−)-1-phenylethanol. This observation is not surprising in light of the lack of correlation between the absolute configuration of the chiral moiety and the helical sense of the resultant chiral/nematic mixture[17] or copolymer.[14] Instead of the atomic number,[16] the effective volume of the substituent group[18] was also adopted in an attempt to define configurational characteristics at an asymmetric carbon center, but the applicability of this scheme was found to be rather limited.[19] Furthermore, it was suggested in Goossen's theory[5] that no correlation between the sign of optical rotation (a molecular property) and helical sense (a supramolecular phenomenon) should be anticipated, which has been observed experimentally for both low molar mass[6]

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[†] Part 1: Chen, S. H.; Tsai, M. L. *Macromolecules* 1990, *23* (11), 5055.

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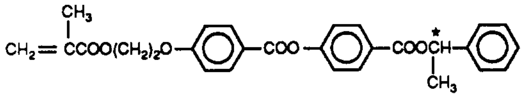
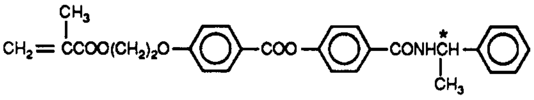
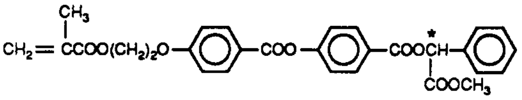
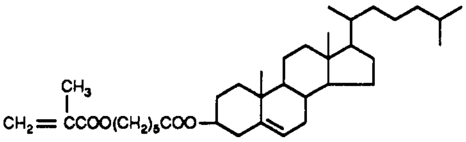
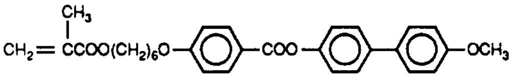
Table I
Chemical Structures and Thermal Properties of the Monomers Used in the Present Study

	transition[a]
Chiral Monomer i Based on (*S*)-(−)-1-Phenylethanol 	K 350 I
Chiral Monomer ii Based on (*S*)-(−)-1-Phenylethylamine 	K 437 I[14]
Chiral Monomer iii Based on (*R*)-(−)-Methyl Mandelate 	K 343 I
Chiral Monomer iv Based on Cholesterol 	K 320 Ch 331 I (299 S, monotropic transition)[15]
Nematogenic Monomer v 	K 357 N 451 I[15]

[a] Symbols for mesophase transitions: K, crystalline; N, nematic; S, smectic; Ch, cholesteric; I, isotropic.

and polymer[14] liquid-crystal systems. Chiral/nematic molecular interaction models[7-11] seem to be a reasonable basis for interpretation in view of the facts that the cholesteric mesophase can be depicted as nematic layers twisted by asymmetric groups[1] and that a neutron diffraction study[20] of fully deuterated *p*-azoxyanisole suggests the nematic mesophase comprising a face-to-face arrangement of linearly extended, planar molecules. The extension of molecular models proposed for low molar mass liquid crystals to polymeric counterparts is admitted by the spacer concept,[13] which serves to decouple the thermodynamic features of mesogenic side groups from those of the polymer backbone. The steric interactions based on the intercalation of biphenyl and/or phenyl rings involving the nematogenic and the chiral moieties are shown in Figure 1, in which X = NH and Y = CH_3 for (*S*)-(−)-1-phenylethylamine, X = O and Y = CH_3 for (*S*)-(−)-1-phenylethanol, and X = O and Y = $COOCH_3$ for (*R*)-(−)-methyl mandelate. It is clearly shown that these three chiral moieties should give rise to a left-handed helix for the next nematic layer on top to maximize a favorable face-to-face arrangement with the chiral component while avoiding the relatively bulky methyl or methoxycarbonyl group. Thus, it appears that the helical sense is determined by the configurational characteristics around the asymmetric carbon center, which does not necessarily follow the definition based on the atomic number[16] or the effective volume[18] of the substituent group.

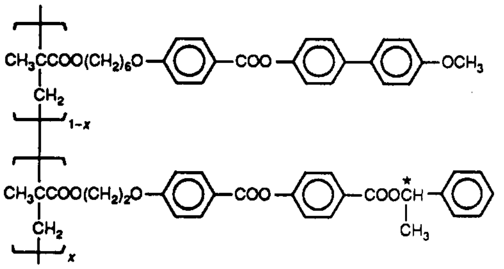
We now turn to the evaluation of helical twisting power (HTP) defined[21] as $\bar{n}(d\lambda_R^{-1}/dx)$ for $x \ll 1$, where $\bar{n}$ is the average index of refraction, λ_R is the selective reflection wavelength, and x is the mole fraction of the chiral comonomer. Using a group contribution method,[22] we found that the indices of refraction for copolymers 1–4 should not differ from each other by more than ±3%. As a result, the slope of the λ_R^{-1} vs x plot at $x \to 0$, as shown in Figure 2, is a reasonable measure of HTP, considering the fact that the experimental uncertainty associated with the λ_R measurement is ±5%. Referring to Figure 2, one finds that the oft-quoted[1] structural similarity between the chiral and nematic components in low molar mass liquid-crystal chemistry plays a significant role in affecting the HTP value in polymeric systems as well. According to Finkelmann and Stegemeyer's[6] analysis based on Goossen's theory[5] the HTP is proportional to the parameter representing the asymmetric dipole–quadrupole interaction between the chiral and the nematogenic components for the copolymers presently investigated. In fact, the order in which the HTP value increases, copolymer 1 > copolymer 2 > copolymer 3, appears to be consistent with what one would expect from the structural similarity point of view. This observation is further buttressed by the fact that cholesterol, a much bulkier chiral moiety also giving a left-handed copolymer, yields an HTP value about 60% lower than 1-phenylethanol with the same nematogenic comonomer. The results from the present study provide some quantitative information on chiral/nematic structural similarity for the optimization of HTP in polymeric systems. However, one should be cautious with a generalization of the argument of "structural similarity" to chiral moieties with significantly different chemical structures. For instance, the HTPs of cholesterol and isopinocampheol, appearing in copolymers V and VI of Part 1, do not follow from what one would expect from structural similarity alone. In a sense, the present work has furnished some fundamental insight, but the interpretation of HTP remains a challenging task.

IV. Conclusions

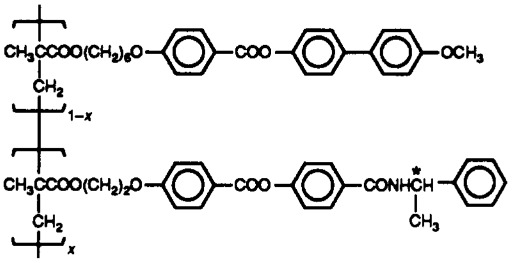
Using (*S*)-(−)-1-phenylethanol and (*R*)-(−)-methyl mandelate as building blocks, we have synthesized and characterized two new series of thermotropic chiral nematic copolymers. Together with the previously reported copolymers containing (*R*)-(+)- and (*S*)-(−)-1-phenyleth-

Table II
Chemical Structures of Chiral Nematic Copolymers Investigated

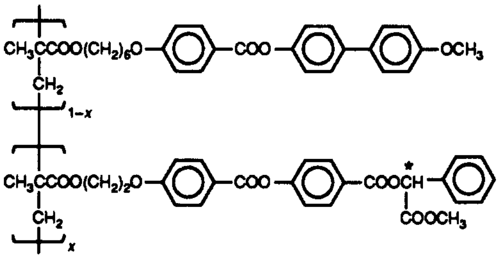
Copolymer 1



Copolymer 2



Copolymer 3



Copolymer 4

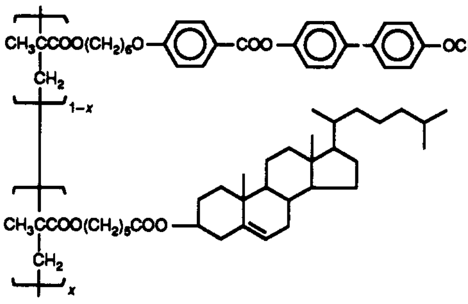


Table III
Structural, Thermal, and Optical Properties of Copolymers 1 and 3

mol fractn chiral moiety x	glass transn temp T_g, K	mesomorphic transn $T_{Ch \to I}$, K	λ_R, nm	$10^4 d\lambda_R^{-1}/dx$, nm^{-1}	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Copolymer 1 Based on (*S*)-(−)-1-Phenylethanol						
0.15	343	500	733	93.6	30.8	1.9
0.19	340	487	543		31.3	1.9
0.24	342	470	450		28.0	1.7
Copolymer 3 Based on (*R*)-(−)-Methyl Mandelate						
0.15	344	483	1193	55.3	23.7	1.6
0.24	347	450	763		34.3	1.6
0.33	353	422	545		46.3	1.7

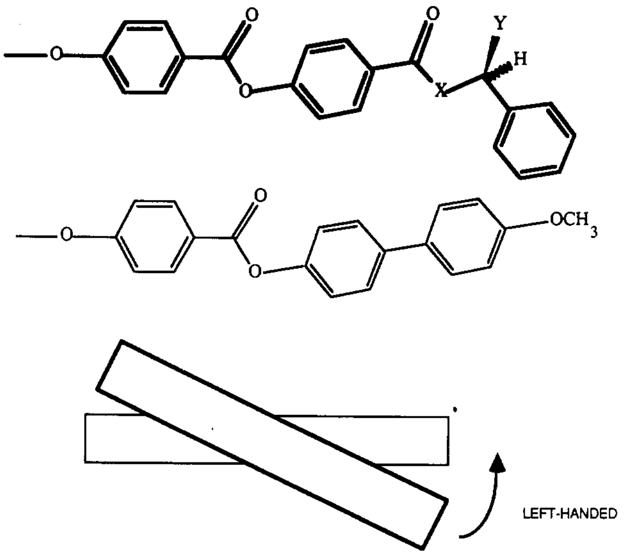


Figure 1. Chiral/nematic molecular interaction model for the interpretation of left-handedness of copolymer 1, X = O and Y = CH_3, copolymer 2, X = NH and Y = CH_3, and copolymer 3, X = O and Y = $COOCH_3$.

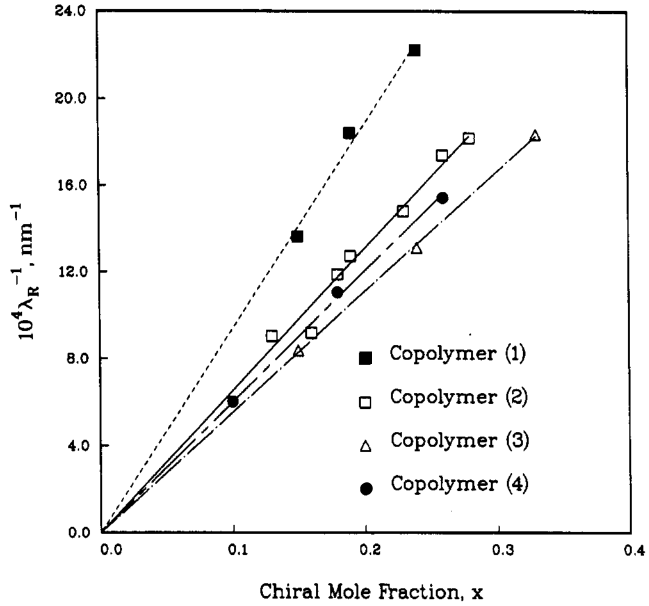


Figure 2. Linear relationship between $1/\lambda_R$ and x for the evaluation of helical twisting power of copolymers 1–4.

ylamine and cholesterol, the issues of helical sense and twisting power have been examined from the molecular interaction point of view. Key observations are summarized as follows: (a) Helical sense in thermotropic side-chain copolymers is determined by the chiral/nematic molecular interactions. In the systems in which long-range interactions (e.g., hydrogen bonding) are absent, steric considerations turn out to be adequate for the interpretation of helical sense. (b) Structural similarity between the chiral and the nematogenic comonomers manifests itself in an enhanced asymmetric dipole–quadrupole interaction, leading to an increased helical twisting power. It is noted that minor structural variations around the asymmetric carbon center may result in considerable changes in the HTP value and that a bulkier chiral moiety does not necessarily give rise to a higher HTP value.

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