New Thermotropic Chiral Nematic Copolymers Using (1*S*,2*S*,3*S*,5*R*)-(+)- and (1*R*,2*R*,3*R*,5*S*)-(−)-Isopinocampheol as Building Blocks

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ABSTRACT: Thermotropic chiral nematic side-chain copolymers were synthesized and characterized by using (1*S*,2*S*,3*S*,5*R*)-(+)- and (1*R*,2*R*,3*R*,5*S*)-(−)-isopinocampheol as the chiral building blocks. The helical twisting power was found to correlate with the volume swept out by the chiral pendant group via rotation for a given nematogenic monomer. However, the enhanced mesomorphic order introduced in both the nematogenic and chiral monomers as a result of an increased extent of conjugation or a shortened spacer length was found to reduce the helical twisting power of the resultant copolymer. Hence, both factors have to be taken into account as the helical twisting power of a copolymer system is to be optimized for a specific application. The present work also generalized our previous observation that the inversion of chirality of the pendant group results in helical sense reversal, although the role of the absolute configuration of the chiral moiety is not yet clearly understood.

I. Introduction

Thermotropic chiral nematic polymers are represented by a class of macromolecular structures in which chiral moieties contribute to the formation of the cholesteric mesophase.[1,2] From the molecular structure point of view, one would expect that a copolymer comprising a nematogenic and a chiral monomer should exhibit cholesteric mesomorphism in view of the common practice in which a chiral nematic material is routinely prepared by mixing a low molar mass nematogen with a chiral dopant.[3,4] Although there exist several empirical rules[5-8] formulated for low molar mass chiral nematics in terms of the helical sense and twisting power in relation to molecular structures, the applicability of these rules to polymeric counterparts has remained inconclusive. In recognition of the tremendous potentials of chiral nematic polymers in emerging optical technologies[9-12] and in view of the scarcity of information[1,2] relating macromolecular structures to relevant optical properties, we have conducted a series of studies on fundamental issues involving helical sense and twisting power in thermotropic side-chain copolymers containing chiral groups other than commonly encountered cholesterol. Cholesterol is known to possess adequate helical twisting power for giving rise to selective reflection wavelength, λ_R, in the visible region; however, it is possible to generate only the left-handed supramolecular structure presumably because of the given set of absolute configurations in naturally occurring cholesterol. Our strategy was to identify pairs of enantiomers that would give rise to strong enough helical twisting power in the yet to be optimized macromolecular structural setting and that would result in both left- and right-handed helical structures, as defined by the sense of the reflected circularly polarized light, to meet the demands of practical applications.

In a recent communcation,[13] we have demonstrated that the inversion of chirality in the side group of a copolymer does lead to the reversal of helical sense using (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine as the chiral building blocks. Furthermore, it was found that the helical twisting power is influenced by the structures of both comonomers, namely, by the consequence of the interplay between the two. These observations have raised the need for systematic investigations of optical property–macromolecular structure relationships with an aim to formulating an empirical basis for molecular design as specific applications arise. With these objectives in mind, we have synthesized and characterized three series of copolymers based on (1*S*,2*S*,3*S*,5*R*)-(+)- and (1*R*,2*R*,3*R*,5*S*)-(−)-isopinocampheol varying in the extent of conjugation (and hence the length of the rigid core) in the chiral monomer structure. The helical twisting power of these new chiral nematic polymers is interpreted in terms of the configurational as well as conformational characteristics and the mesomorphic order of both the chiral and the nematogenic monomers; relevance is also made to the classical cholesterol-containing copolymers.

II. Experimental Section

The chemical structures and phase transition temperatures of the methacrylate monomers employed in the present work are summarized in Table I; literature values for the mesophase transition temperatures are also included for comparison wherever possible. All the monomers were synthesized following the procedures reported in the literature[14-17] except those containing commercially available, optically pure isopinocampheol. Figure 1 sketches the reaction scheme for the synthesis of chiral monomers containing isopinocampheol. All of the following reagents were used as received from Aldrich Chemical Co.: 4-hydroxybenzoic acid (99%), 4-hydroxycinnamic acid, predominantly trans (98%), (1*S*,2*S*,3*S*,5*R*)-(+)-isopinocampheol (99%), (1*R*,2*R*,3*R*,5*S*)-(−)-isopinocampheol (98%), and cholesterol (98%). The four-step procedure of Gray et al.[18] was followed to synthesize 4-(4-hydroxyphenyl)benzoic acid.

Copolymerization of a nematogenic and a chiral monomer was accomplished in anhydrous tetrahydrofuran in the presence of azobis(isobutyronitrile) at 333 K for 48 h in a nitrogen atmosphere. The copolymers were isolated and repeatedly precipitated from acetone or methanol until the monomers were completely removed and then dried in a vacuum oven for several days prior to analysis. The structures of the copolymers synthesized for the present investigation are summarized in Figure 2.

The chemical structures of both monomers and copolymers were elucidated with IR (710B, Perkin-Elmer) and proton NMR (QE-300, GE) spectroscopy. The mesophase transition temperatures were determined with a differential scanning calorimeter (DSC-4, Perkin-Elmer) at a scan rate of 20 °C/min while continuously purged either with nitrogen for normal operations or helium for low-temperature runs; the inflection point was taken

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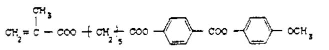
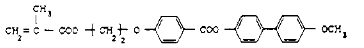
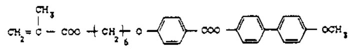
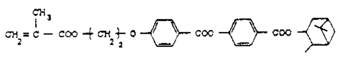
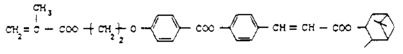
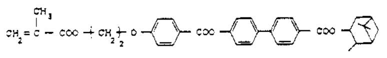
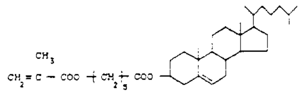
Table I
Chemical Structures and Phase Transition Temperatures (K) for Monomers[a]

Nematogenic component		
	(i)	K 327.2 I (308.6 N)
	(ii)	K 381.0 N 483.0 I [K 381.0 N 484.0 I][b]
	(iii)	K 356.5 N 451.0 I [K 358.0 N 456.0 I][c]
Chiral component		
	(iv)	K 349.0 I
	(v)	K 372.0 I
	(vi)	K 384.0 Ch 411.0 I
	(vii)	K 320.0 Ch 330.5 I (299.0 S) [K 321.2 Ch 330.3 I (298.0 S)][d]

[a] Symbols for mesophase transitions: K, crystalline; N, nematic; S, smectic; Ch, cholesteric; I, isotropic. Monotropic transitions represented by parentheses. [b] Finkelmann, H.; Ringsdorf, H.; Wendorff, J. H. *Makromol. Chem.* **1978,** *179,* 273. [c] Finkelmann, H.; Portugall, M.; Ringsdorf, H. *Polym. Prepr.* **1978,** *19* (2), 183. [d] Shannon, P. J. *Macromolecules* **1983,** *16,* 1677.

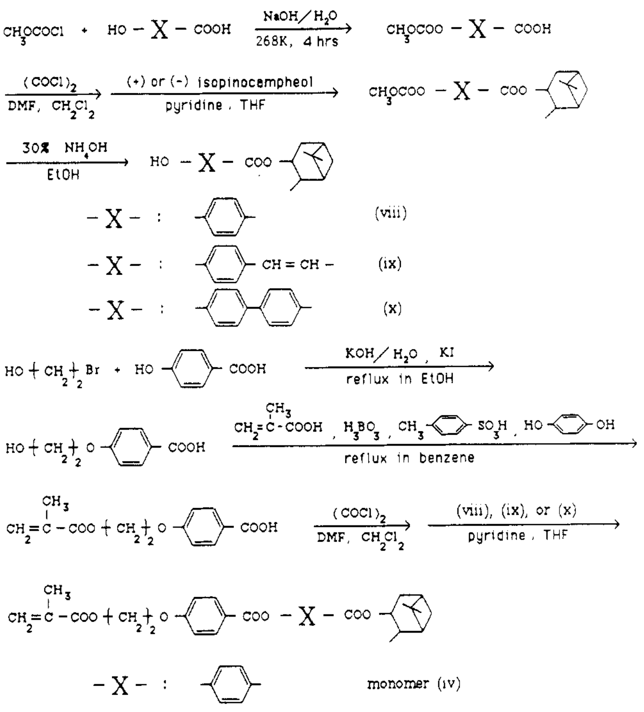


Figure 1. Reaction scheme for the synthesis of the chiral monomers containing (1*S*,2*S*,3*S*,5*R*)-(+)- and (1*R*,2*R*,3*R*,5*S*)-(−)-isopinocampheol.

as T_g. A polarizing optical microscope (Leitz Orthoplan-Pol) equipped with a programmable hot stage (FP52, Mettler) was used to identify mesomorphism upon heating or cooling. Normally, thermal annealing at selected elevated temperatures for 2 days or so was required to increase the domain size for mesophase identification of copolymers.

The determination of molecular weight distribution, from which both $\bar{M}_n$ and $\bar{M}_w$ could be calculated, was accomplished in a size

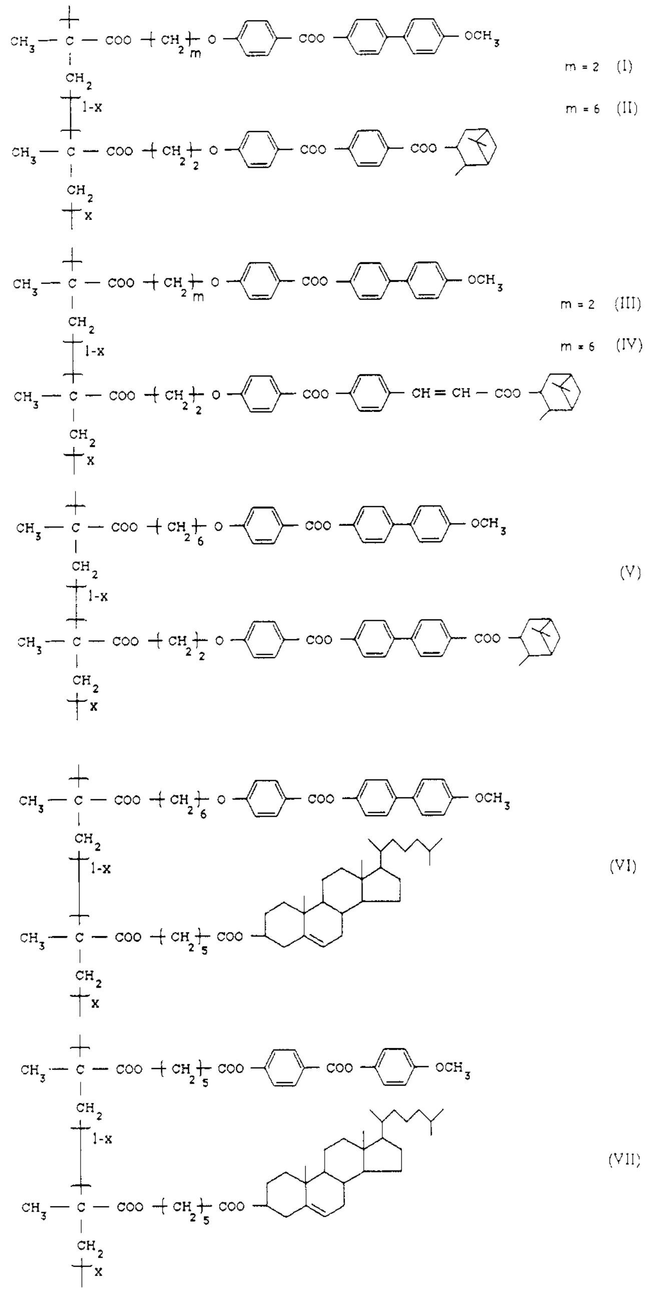


Figure 2. Structures of the thermotropic chiral nematic copolymers synthesized for the present study.

exclusion chromatography system constructed with an HPLC metering pump (Constametric III, Milton Roy), two PLgel columns in series (500 and 10 000 Å, Hewlett-Packard) housed in a column oven (Jones Chromatography), and a UV differential absorbance detector (UV III Monitor, Milton Roy) set at 254 nm. The selective reflection wavelength λ_R was determined on a UV-vis-near-IR spectrophotometer (Lambda 9, Perkin-Elmer). Prior to the spectrophotometric measurements, optical elements (prepared by placing about 20 mg of copolymer products between a pair of soda lime glass substrates separated with 13-μm-thick Kapton spacers) were annealed at temperatures close to $0.95T_I$, T_I being the isotropic transition temperature, for a day or two before quenching to room temperature. The determination of λ_R was found to be reproducible to within ±5% of the mean on repeated measurements. The handedness of the chiral nematic copolymers was further determined by spectrophotometric measurements of the so-prepared optical elements placed in series with those made of a commercially available low molar mass nematic host and a chiral dopant mixed at a ratio that gives rise to the desired value for λ_R with known handedness. For example, low molar mass chiral nematics containing nematogen E-7 and chiral additive CB-15 (both from BDH Ltd.) are known to exhibit a right-handed helical structure. The determination of

Table II
Structural Characteristics and Thermal Properties of Copolymers I and II

x^a	T_g,[b] K	$T_{\mathrm{Ch}\to\mathrm{I}}$,[c] K	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Copolymer I with (1*S*,2*S*,3*S*,5*R*)-(+)-Isopinocampheol				
0.17	363	514	12.5	1.44
0.28	345	475	13.6	1.65
0.38	366	460	22.2	2.74
0.49	367	443	37.2	2.62
0.59	362	424	36.3	2.50
0.70	374	417	41.8	2.09
0.75	364	380	32.1	1.92
Copolymer II with (1*R*,2*R*,3*R*,5*S*)-(−)-Isopinocampheol				
0.41	331	439	22.2	2.49
0.48	338	421	22.0	2.26
0.59	349	420	19.0	2.20
0.69	355	404	23.2	2.12

[a] Mole fraction of chirality; determined with integration on proton NMR spectra. [b] Glass transition temperature. [c] Mesomorphic transition.

Table III
Structural Characteristics, Thermal Properties, and the Observed Values of λ_R for Copolymers III, IV, and V

x^a	T_g,[a] K	$T_{\mathrm{Ch}\to\mathrm{I}}$,[a] K	λ_R, nm	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Copolymer III with (1*S*,2*S*,3*S*,5*R*)-(+)-Isopinocampheol					
0.16	360	504	[b]	11.0	1.45
0.26	357	488	2817	15.3	1.84
0.38	364	463	2176	26.2	2.38
0.46	353	451	1735	19.4	1.76
0.49	380	amorph		29.1	2.44
Copolymer IV with (1*R*,2*R*,3*R*,5*S*)-(−)-Isopinocampheol					
0.35	326	428	1936	23.1	2.19
0.44	336	411	1511	24.4	2.23
0.54	342	398	1151	26.4	2.26
Copolymer V with (1*S*,2*S*,3*S*,5*R*)-(+)-Isopinocampheol					
0.31	345	520	[b]	21.3	1.90
0.40	352	513	2908	19.7	1.80
0.51	348	512	1996	23.3	1.65
0.60	356	519	1572	28.4	1.88

[a] See Table II footnotes. [b] λ_R outside of the wavelength region on a Lambda 9 spectrophotometer although the cholesteric mesophase was observed under a polarizing optical microscope.

handedness was further assisted by the polysiloxane series[19] furnished by Dr. F. H. Kreuzer of the Consortium für Elektrochemische Industrie (West Germany). The polysiloxane samples provided a wide range of λ_R from 442 to 2200 nm with left-handed helical sense.

III. Results and Discussion

The chemical structures of the copolymers as summarized in Figure 2 should permit one to address the following questions:

(1) How does the extent of conjugation as well as the attendant configurational characteristics built in the chiral monomer affect the helical twisting power for a given nematogenic comonomer?

(2) How does the mesomorphic order of the nematogenic and chiral monomers influence the helical twisting power of the resultant copolymer?

(3) Does the spacer length in the nematogenic monomer play any role in the determination of the helical twisting power?

(4) Is there any correlation between the chirality of one of the pendant groups and the helical sense in a copolymer?

The structural characteristics, the thermal properties, and the observed values of λ_R for copolymer series I–VII are presented in Tables II–IV. To address the first question raised above, it is noted that the increased anisotropy (the length to the diameter ratio) and the increased extent of conjugation contribute to the enhanced clearing temperature and to the formation of the cholesteric mesophase as one examines the thermal behaviors of monomers iv, v, and vi as presented in Table I. The copolymers comprising the nematogenic monomer ii or iii and chiral comonomers iv and v with an increasing extent of conjugation were found to exhibit a higher helical twisting power. For instance, although the cholesteric mesophase could be identified on optical elements prepared with copolymers I and II with polarizing optical microscopy, the λ_R values appear to have fallen beyond the long-wavelength limit of 3200 nm on the Lambda 9 spectrophotometer. The pitch of a cholesteric mesophase is essentially a measure of the angular displacement between adjacent nematic layers. With increased volume swept out by the *trans*-4-hydroxycinnamic acid moiety via rotation in chiral monomer v as compared to iv, copolymers III and IV give rise to λ_R in the range from 2817 to 1151 nm as shown in Table III. Following this line of argument, one would have expected that copolymer V should possess a helical twisting power intermediate between those of copolymers II and IV because of the linear character of the biphenyl moiety, which is consistent with what is shown in Figure 3, where the slope of $1/\lambda_R$ vs x represents a measure of the helical twisting power.

An alternative argument is that for a given nematogenic monomer, the chiral comonomer that possesses higher mesomorphic order would yield a copolymer with reduced helical twisting power as one compares copolymer V with copolymer IV. It is suspected that the reduced helical twisting power with copolymer V might have originated from what Shibaev and Freidzon[2] referred to as the tendency toward smectogenicity suppressing the helical twisting power although no smectic mesophase was observed in addition to the cholesteric mesophase as reported in Table III. The failure to detect the smectic mesophase prior to the cholesteric mesophase in the

Table IV
Structural Characteristics, Thermal Properties, and the Observed Values of λ_R for Copolymers VI and VII

x^a	T_g,[a] K	$T_{\mathrm{S}\to\mathrm{Ch}\to\mathrm{I}}$,[a] K		λ_R, nm	$10^{-3}\bar{M}_w$	$\bar{M}_w/M_n$
Copolymer VI						
0.10	316	393	515	1659	21.7	1.74
0.18	313	411	500	905	14.5	1.48
0.26	313	424	497	648	22.9	1.58
Copolymer VII						
0.08	313		379	1244	14.0	1.13
0.17	323		393	642	16.5	1.18
0.21	314		386	534	14.2	1.12

[a] See Table II footnotes.

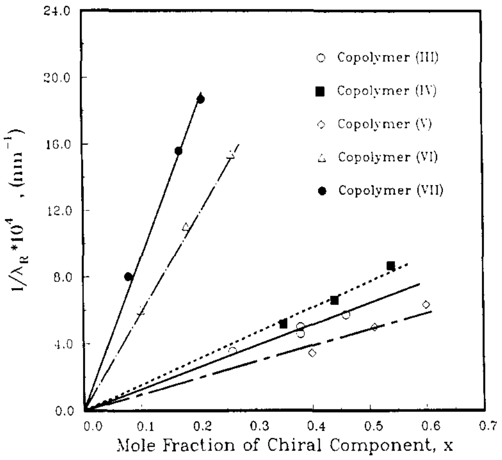


Figure 3. $1/\lambda_R$ as a function of x for copolymers III–VII.

temperature scale with the DSC technique is not surprising in view of the observation made by Freidzon et al.[20] on methacrylate copolymers. It remains to be verified if the same argument applies to situations in which a given chiral monomer is copolymerized with two nematogenic comonomers with different mesomorphic order. A case in point is chiral monomer vii copolymerized with nematogenic monomer iii vs i, the former showing a regular nematic to isotropic transition upon heating while the latter a monotropic isotropic to nematic transition upon cooling. In other words, a nematogenic monomer with enhanced mesomorphic order is expected to yield copolymers with a reduced helical twisting power for a given chiral comonomer. This prediction is borne out in Figure 3 in which copolymer VII is found to possess a higher helical twisting power than copolymer VI. Thus, one could answer the second question by concluding that the higher the mesomorphic order of either nematogenic or chiral monomer, the lower the helical twisting power of the resulting copolymer. Such a conclusion does not seem to contradict the observation made above for copolymers III and IV as opposed to copolymers I and II for the reason that neither monomer iv nor v possesses mesomorphic character. As a matter of fact, the volume swept out by the chiral pendant group seems to play a predominant role in helical twisting power in this case.

The effect of the spacer length in the nematogenic monomer on the helical twisting power for a given chiral comonomer is revealed in Figure 3 in terms of the slopes of $1/\lambda_R$ vs x for copolymers III and IV. It is clearly demonstrated that the longer spacer length yields the higher helical twisting power, an observation consistent with the conclusion reached above in terms of the role of mesomorphic order of monomers in the determination of helical twisting power. Simply put, monomer ii possesses a more stable nematic mesophase than monomer iii as indicted in Table I. Hence, for the given chiral comonomer v, monomer ii is expected to form a copolymer, i.e., III, possessing a lower helical twisting power than copolymer IV synthesized from monomer iii. However, an exception to this general observation was reported by Finkelmann and Rehage[21] on siloxane-based copolymers. Finally, it was found that (1*S*,2*S*,3*S*,5*R*)-(+)-isopinocampheol yields right-handed helices in copolymers III, IV, and V and that (1*R*,2*R*,3*R*,5*S*)-(−)-isopinocampheol yields left-handed counterparts in copolymers with otherwise identical structures. In a recent communication,[13] we have also reported that (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine yield right- and left-handed helixes, respectively. However, none of these observations appear to constitute a sound basis for the correlation between the absolute configuration of the chiral moiety and the handedness of the copolymer on the supramolecular scale. It is noted in passing that the sense of the specific optical rotation of the chiral moiety has been demonstrated to play no role in the helical sense of the cholesteric mesophase.[13] Nevertheless, that the inversion of chirality leads to opposite handedness does seem to have a solid empirical foundation.

IV. Summary

Using (1*S*,2*S*,3*S*,5*R*)-(+)- and (1*R*,2*R*,3*R*,5*S*)-(−)-isopinocampheol, we have synthesized a series of thermotropic chiral nematic copolymers with a varying extent of conjugation built into the chiral monomer. Along with the observations made for the classical cholesterol-containing copolymers, we summarize the present study in what follows:

(1) With a given nematogenic monomer, an increased volume swept out by the chiral pendant group via rotation contributes to the enhanced helical twisting power.

(2) Enhanced mesomorphic order as a result of an increased length of the rigid core or a shortened spacer length of both the nematogenic and chiral monomers tends to suppress the helical twisting power.

(3) It is a general observation that the inversion of chirality in the side group does lead to opposite handedness in the helical sense of the cholesteric mesophase. The question of how the helical sense correlates with the absolute configuration of the pendant chiral moiety has yet to be carefully addressed.

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