1908 *Macromolecules* **1990,** *23,* 1908-1911

Helical Sense in Thermotropic Liquid Crystal Copolymers in Relation to the Structure of a Pendant Chiral Moiety

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ABSTRACT: Chiral nematic copolymers based on optically active cholesterol, dihydrocholesterol, and (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine were synthesized and characterized for the investigations of thermotropic and optical properties. With cholesterol and dihydrocholesterol possessing largely the same absolute configurations and molecular sizes but opposite signs in specific optical rotation, they both give left-handed helical structures. However, cholesterol shows a helical twisting power 80% higher than dihydrocholesterol in otherwise identical macromolecular structural settings. Although helical sense does not appear to correlate with the sign of $[\alpha]_D$ of the precursor chiral compound as suggested by the observations of cholesteryl and dihydrocholesteryl copolymers, the inversion of chirality in the pendant group, (*R*)-(+)- vs (*S*)-(−)-1-phenylethylamine, does lead to the opposite handedness in the resultant helical structure. To better understand the structure-property relationships involving helical sense and twisting power, systematic studies of the roles played by both nematogenic and chiral structures as well as other structural features of the comonomers should be conducted.

1. Introduction

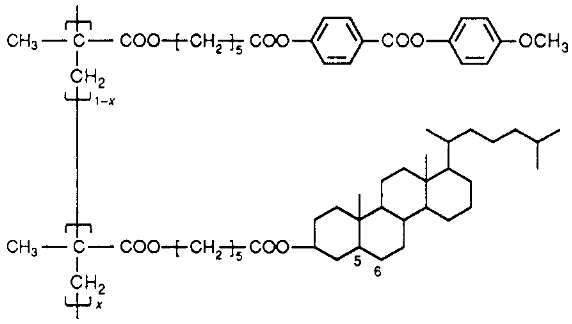
Because of the unique property of selective wavelength reflection, chiral nematic polymers have recently been demonstrated to be capable of forming optical notch filters.[1,2] This class of polymers are also potentially useful for the fabrication of such optical devices as isolators, beam splitters, and beam apodizers.[3] Moreover, they are ideal candidates for optical information storage based on mesomorphic transitions and the accompanying changes in the index of refraction and optical birefrigence.[4-6] Most of these applications require polymers capable of forming both right- and left-handed helical structures upon proper thermal annealing.

Although there exist a number of polymers reported to form left-handed helical structures,[7-10] there is a paucity of right-handed polymers, the only known examples being chemically modified poly(γ-benzyl D- or L-glutamate)[11] and (hydroxypropyl)cellulose.[12] In these two series of right-handed polymers, chiral centers reside in the polymer backbone. In the case of glutamate copolymers the inversion of chirality has been shown to lead to opposite handedness in the helical structure.[10,13] The key issue to be addressed in this paper is whether or not the same observation is applicable to polymers in which chiral centers reside in side groups. Methacrylate copolymers incorporating optically active cholesterol, dihydrocholesterol, and a pair of enantiomers, (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine, were synthesized and characterized to examine the possible correlation between the absolute configuration of a pendant chiral group and helical sense at the supramolecular level.

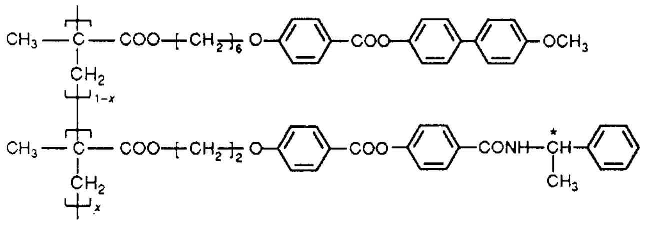
It is noted that cholesterol has been the most commonly encountered pendant chiral moiety; both homopolymers[14-16] and copolymers[9,17,18] with a pendant cholsteryl group have been reported. Homopolymers[15] carrying a pendant dihydrocholesteryl group has also been synthesized. To the best of our knowledge, no chiral nematic copolymers based on dihydrocholesterol have been investigated to date. Furthermore, helical sense in relation to the specific optical rotation of the chiral pendant group has not been examined. Finkelmann and his coworkers[19] reported a series of side-chain copolymers with a Schiff's base linkage to optically pure 1-phenylethylamine, but the issue of helical sense of the copolymer products in relation to the chirality of the side group was not clearly addressed. Hence, the main goal of this work is to examine the roles that specific optical rotation and absolute configuration of the chiral moeity play in the determination of helical sense. We remark in passing that an amide linkage was adopted here because of the lack of stability against temperature or moisture[20,21] with Schiff's bases.

2. Experimental Section

Copolymers synthesized for the present study include the following:



I: C═C at C₅ and C₆
II: C—C at C₅ and C₆



III

Five methacrylate monomers were needed for the synthesis of

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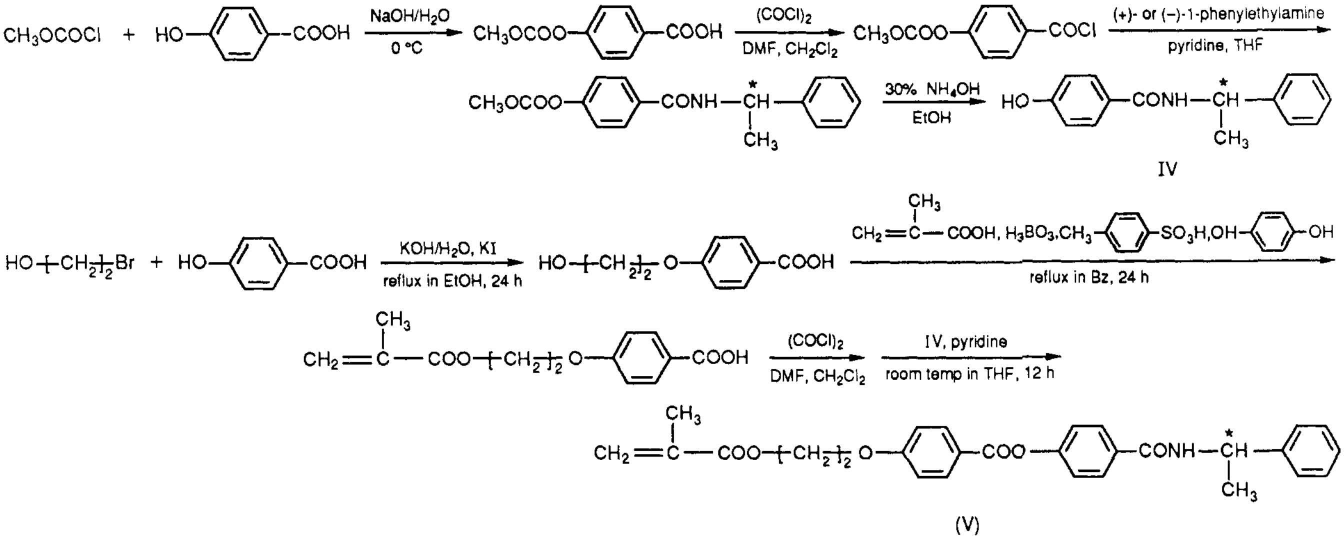
Scheme I
Synthesis of the Chiral Methacrylate Monomer Involving 1-Phenylethylamine



copolymers I–III. With the exception of the monomer involving 1-phenylethylamine, standard experimental procedures reported in the literature[19,22–24] were followed. The synthesis of the chiral methacrylate based on 1-phenylethylamine was accomplished via Scheme I. The chemical structure of V was verified with mass spectrometery (VG 7035), FTIR (20 SXC, Nicolet), and proton NMR (QE-300, GE) spectroscopy, and the crystal to isotropic transition was observed to occur at 437 K under polarizing optical microscope (Leitz Orthoplan-Pol) equipped with a Mettler FP52 Microthermal system.

Radical copolymerization initiated with azobis(isobutyronitrile) was carried out in either benzene or anhydrous tetrahydrofuran at 333 K for 1 day or so under a nitrogen atmosphere. The copolymer products were isolated from the reaction mixture by precipitation with an excess of nonsolvents including diethyl ether, methanol, and acetone and further purified by repeated dissolution–precipitation cycles. Copolymer structures were then verified with IR and proton NMR spectroscopy, and a size-exclusion chromatography system with a UV differential absorbance detector was used to characterize molecular weight distribution from which the weight-average molecular weights were calculated. Polydispersity indices, $\bar{M}_w/\bar{M}_n$, were found to be in the range from 1.5 to 2 for all copolymer series. Thermal properties including glass and mesophase transition temperatures were determined with a differential scanning calorimeter (DSC-4, Perkin-Elmer) at a scan rate of 20 C/min under a nitrogen purge of 20 mL/min.

Optical elements for the determination of selective reflection wavelength λ_R on a UV–vis–near-IR spectrophotometer (Lambda 9, Perkin-Elmer) were prepared by placing about 20 mg of copolymer products between a pair of soda lime glass substrates (50 mm in diameter and 1.6 mm thick) with 13 μm thick Kapton spacers. Prior to spectrophotometric measurements, optical elements were annealed at temperatures in the range from 0.86 to $0.96T_{c,i}$ for an hour or two followed by quenching to room temperature. The determination of λ_R was found to be reproducible to within ±3% of the mean on repeated measurements. Finally, the handedness of the annealed helical structure was determined by a spectrophometric measurement of the so prepared optical element placed in series with the one made of a commercially available low molar mass nematic host and a chiral compound mixed at a ratio that gives rise to the same λ_R with known handedness. For instance, nematic E-7 and chiral additive CB-15, the low molar mass materials available from BDH in England, are known to exhibit right-handed cholesteric sense in the wavelength region of interest here.

Table I
Thermotropic Property and Selective Reflection Wavelength for Copolymers I, II, and III[a-c]

mole fractn of chiral moiety, x	glass transitn, T_g, K	mesomorphic transitn (K)		λ_R, nm	$10^{-3}\bar{M}_w$
		S → Ch	Ch → I		
		Copolymer I			
0.08	313		379	1244	16.7
0.17	323		393	642	33.6
0.21	314		386	534	17.7
		Copolymer II			
0.20	316	351	386	954	29.0
0.29	310	363	387	680	26.6
0.40	311	363	382	560	19.8
		Copolymer III with (*R*)-(+)-1-Phenylethylamine			
0.13	346		487	1105	20.9
0.18	344		477	842	25.4
0.23	355		467	675	25.6
0.28	351		455	550	28.1
		Copolymer III with (*S*)-(−)-1-Phenylethylamine			
0.16	342		491	1088	24.2
0.19	345		476	785	20.8
0.26	354		459	575	22.2

[a] x values were determined with integration on proton NMR spectra. [b] $\bar{M}_w$ varies from one batch to the other because of the difference in initiator to monomer ratio. [c] Ch, cholesteric; S, smectic; I, isotropic.

3. Results and Discussion

The thermotropic and optical properties of the three copolymer series under present investigation are summarized in Table I. In the comparison of I to II involving cholesteryl and dihydrocholesteryl groups, respectively, we make two observations. (a) While copolymer I did not show the smectic mesophase under the hot-stage polarizing optical microscope, the smectic to cholesteric transition was clearly identifiable with both optical microscopy and differential scanning calorimetry for copolymer II. (b) Cholesterol has a helical twisting power 80% higher than dihydrocholesterol in identical macromolecular structural settings. The intriguing point is that cholesterol and dihydrocholesterol possess about the same overall absoltue configurations,[25] while they show opposite signs in their specific optical rotations: $[\alpha]^{24}{}_D$ −40° (c = 2, $CHCl_3$), cholesterol; $[\alpha]^{21}{}_D$ +23.8° (c = 1.3, $CHCl_3$), dihydrocholesterol. Using a low molar mass nematic host and a chiral compound mixed at a ratio that gives rise to the desired λ_R with known handedness, it was determined that both I and II present left-handed

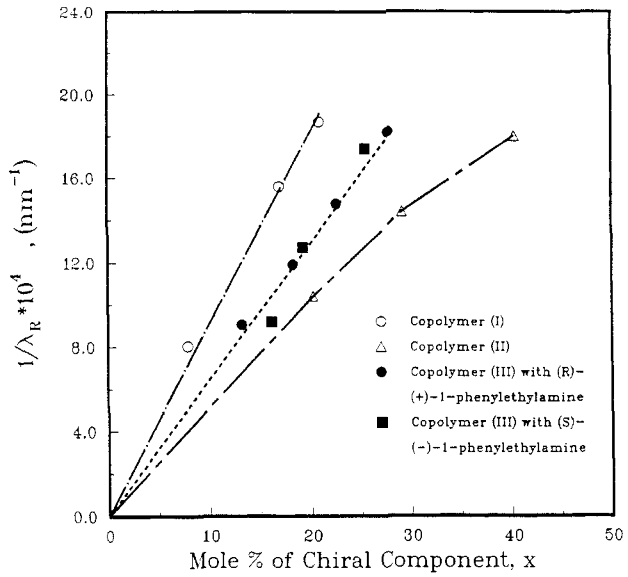


Figure 1. λ_R^{-1} as a function of x for copolymers I, II, and III.

helical structures. Thus, other structural features being identical, the sign of the specific optical rotation of the pendant chiral group does not seem to affect helical sense in thermotropic copolymers. This observation leaves the absolute configuration of the pendant chiral group to be further examined. One of the approaches to achieve this task is to use a pair of optically pure enantiomers as the pendant group, (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine being the examples to be pursued in what follows.

Results for the two series of copolymer III are also presented in Table I. There exists a wide temperature range for the existence of the cholesteric mesophase, and the selective reflection wavelength was found to be practically independent of temperature within an experimental uncertainty of ±3% associated with the determination of λ_R at annealing temperatures up to 433 K. It was also found that the inversion of chirality of the pendant group leads to the opposite handedness in the resultant helical structure; the (*R*)-(+) and (*S*)-(−) enantiomers were found to give rise to a right- and left-handed helix, respectively. Note that helical sense versus inversion of chirality is a relative issue. It would be interesting to find out if there exists a correlation between the absolute configuration of the pendant chiral moiety and the helical sense at the supramolecular level. Furthermore, one should investigate structural variations outside of the chiral moiety that might lead to changes in helical sense. These are some of the questions that one must address to fully understand structure-property relationships involving chiral nematic polymers in view of the fact that the cholesteric sense is not predictable with the chirality of the optically active dopant in a nematic host[26] for low molar mass liquid crystals.

Finally, λ_R^{-1} as a function of x is plotted up in Figure 1 for the three copolymer series. Since the temperature dependences of λ_R were found to be insignificant, the helical twisting power can be determined from the slope, ($d\lambda_R^{-1}/dx$) as $x \rightarrow 0$, in light of the fact that the average refractive index $\bar{n}$ is not expected to differ by more than 3% from one copolymer to the other as estimated via group contribution methods.[27] It is clear that 1-phenylethylamine possesses a helical twisting power intermediate between cholesterol and dihydrocholesterol. It thus appears that the helical twisting power is a function of the structures of both nematogenic and chiral comonomers. Extensive structure-property investigations are warranted to identify the factors affecting the helical twisting power in view of the fact that neither molecular optical rotation, (MW)$[\alpha]_D$, nor molecular size of the precursor chiral building blocks seems to correlate with the observed trend in helical twisting power. It is also well-known in the liquid crystal literature that the helical twisting power of a given chiral dopant may vary considerably with the chemical structure of the nematic host,[28] suggesting that the helical twisting power in polymeric systems may very well depend on the structures of both chiral and nematogenic comonomers. We will continue to report the results from our laboratory in future papers.

4. Conclusions

We have synthesized thermotropic chiral nematic copolymers using optically pure cholesterol, dihydrocholesterol, and (*R*)-(+)- and (*S*)-(−)-phenylethylamine as the pendant chiral moieties. The following observations were made of the thermotropic and optical properties.

(a) While dihydrocholesteryl copolymers show the smectic mesophase besides the cholesteric mesophase with hot-stage polarizing optical microscopy and differential scanning calorimetry, cholesteryl copolymers exhibit only the cholesteric mesophase.

(b) Although both cholesterol and dihydrocholesterol possess largely the same absolute configurations at all asymmetric centers and more or less the same molecular size, the helical twisting power determined with ($d\lambda_R^{-1}/dx$) as $x \rightarrow 0$ in copolymer I is 80% higher than that in copolymer II.

(c) Cholesterol and dihydrocholesterol have opposite signs in specific optical rotation, $[\alpha]_D$, but both copolymers I and II give rise to left-handed helices in otherwise identical macromolecular structural settings, suggesting that helical sense does not correlate with the sign of $[\alpha]_D$ of the precursor chiral compound.

(d) Using a pair of enantiomers, (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine, it was established that the inversion of chirality in the pendant group does lead to opposite handedness in the resultant helical structures presented by the thermotropic copolymers.

(e) The fact that copolymer III shows a helical twisting power intermediate between copolymers I and II implies that the helical twisting power is likely to be a consequence of the interaction between nematogenic and chiral comonomers.

Acknowledgment. We wish to acknowledge helpful discussions with S. D. Jacobs and K. L. Marshall of the Laboratory for Laser Energetics, University of Rochester. This work was supported by Kaiser Electronics and the National Science Foundation under Grant CBT-8714924. Partial support was also provided by the U.S. Army Research Office under Contract DAAL03-86-K-0173, the U.S. Department of Energy Division of Inertial Fusion under Agreement No. DE-FC03-85DP40200, and the Lader Fusion Feasibility Project at the Laboratory for Laser Energetics which has the following sponsors: Empire State Electric Energy Research Corp., New York State Energy Research and Development Authority, Ontario Hydro, and the University of Rochester. Such support does not imply endorsement of the content by any of the above parties.

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Anionic Ring-Opening Polymerization of 1,1,3-Trimethyl-1-silacyclopent-3-ene. Effect of Temperature on Poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene) Microstructure

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Received August 7, 1989; Revised Manuscript Received October 10, 1989

ABSTRACT: 1,1,3-Trimethyl-1-silacyclopent-3-ene (I) undergoes anionic ring-opening polymerization on treatment with *n*-butyllithium and HMPA cocatalysts in THF to yield poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene) (II). Comparison of ^{1}H, ^{13}C, and ^{29}Si NMR spectra of II with those of model compounds, (*Z*)- and (*E*)-2-methyl-1,4-bis(trimethylsilyl)-2-butene (IV), permits assignment of polymer II microstructures. When the polymerization of I is conducted at −42 °C, the NMR spectra of II are consistent with a polymer in which *cis*-1,4-isoprene units are joined to dimethylsilylene units. A 1:2:1 distribution of head-to-head, head-to-tail, and tail-to-tail arrangements of adjacent *cis*-1,4-isoprene units is found. On the other hand, when the polymerization is conducted at −78 °C, the microstructure of II is predominantly head-to-tail. The mechanism of polymerization, which may account for the observed regioselectivity, is discussed.

We have previously reported that anionic ring-opening polymerization of 1,1,3-trimethyl-1-silacyclopent-3-ene (I) catalyzed by *n*-butyllithium/hexamethylphosphoramide (HMPA) or methyllithium/tetramethylethylenediamine (TMEDA) in THF solvent at −40 °C leads to poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene) (II).[1] While the microstructure of the closely related system, poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (III) was assigned on the basis of comparison of ^{13}C NMR chemical shifts with model compouunds,[2] the assignment of the microstructure of II was made on the basis of less firm evidence. Several experiments have led us to more thoroughly study this system. Chief among these was the observation that when we conducted the polymerization at different temperatures, the intensity ratio of the ^{1}H and ^{13}C NMR signals assigned to the methyl groups bonded to silicon changed (Figures 1 and 2).

To clarify this situation, we have prepared both (*Z*)- and (*E*)-2-methyl-1,4-bis(trimethylsilyl)-2-butene [(*Z*)-IV and (*E*)-IV]. While these model compounds are known,[3] neither high-field ^{1}H, ^{13}C, nor ^{29}Si NMR spectra of them have been reported. The assignment of ^{13}C NMR chemical shifts was done on the basis of ^{1}H-coupled ^{13}C NMR spectra. The significant difference in the ^{13}C chemical shift of the methyl and the proximate methylene carbons bonded to a cis carbon–carbon double bond compared to those bonded to a trans carbon–carbon double bond should be noted (Figures 3–5).

Of great significance, we have found that when I is treated with *n*-butyllithium/HMPA cocatalysts in THF

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