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A Comparative Study of Helical Sense and Twisting Power in Low Molar Mass and Polymeric Chiral Nematics

Sushil Krishnamurthy[†] **and Shaw H. Chen***

Department of Chemical Engineering and Laboratory for Laser Energetics, University of Rochester, Rochester, New York 14627-0166

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ABSTRACT: The issues of helical sense and helical twisting power (HTP) have been addressed using low molar mass analogues of chiral nematic copolymers containing (*S*)-(+)-2-methoxy-2-phenylethanol, (*S*)-(−)-1-phenylethanol, and (*R*)-(−)-methyl mandelate. As reported by other workers, it is found that the empirical rules proposed by Gray et al. for interpreting helical sense are limited in scope. However, the handedness observed in the new copolymeric system and that of the copolymers reported earlier are consistent with the low molar mass counterparts. The HTP's of chiral nematic mixtures based on (*S*)-(−)-1-phenylethanol and (*R*)-(−)-methyl mandelate are much lower than those of the corresponding copolymeric structures reported earlier, which is attributed to hindered rotation imposed by polymerization. In contrast, chiral nematic mixtures containing (*S*)-(+)-2-methoxy-2-phenylethanol show an HTP value only slightly lower than that of the copolymer. In addition, for all three systems, the selective reflection wavelength is observed to increase with decreasing temperature, consistent with Keating's model and with the molecular statistical theory of Kimura et al.

I. Introduction

The current understanding of the cholesteric mesophase in terms of helical sense and twisting power (HTP) has derived from experimental investigations,[1,2] molecular theories[3–5] and models,[6–8] and empirical rules[9] that contribute to potential applications to optical device fabrication[10–12] and optical information storage.[12] Although the molecular theory formulated by Goossens[4] was successfully employed to interpret several chiral nematic system parameters,[13] many existing theories reported in the literature do not allow a ready comparison with experimental results. However, in the case of nonsteroidal chiral compounds, molecular models incorporating both steric and hydrogen-bonding interactions have been successfully employed to rationalize the observed helical sense in a number of doped chiral nematic systems.[6–8] Furthermore, the empirical SED-ROD and SOL-REL rules proposed by Gray et al.[9] were found to be applicable to a number of cholesteric[9] as well as induced cholesteric[14–16] systems. These rules have also been corroborated, with limited success, with molecular mechanics calculations[16,17] on a series of alkylbiphenyl compounds.

The spacer concept,[18] which was introduced to decouple the motion of mesogenic pendant groups from that of the polymer backbone, led to the development of the field of side-chain liquid crystal polymers. By a suitable choice of this parameter, it was possible to extend the principles of mesophase formation in low molar mass liquid crystals to polymeric systems, based on which a number of liquid crystal polymers showing the nematic, smectic, and cholesteric mesophases have been synthesized and characterized.[19,20] However, the spacer provides only a partial decoupling,[21,22] and in cases where the pendant groups are linked end-on to the spacer, the resulting polymers tend to form higher order mesophases than the corresponding monomers, accompanied by a shift toward higher mesomorphic transition temperatures.[23] Although some investigations exist in the literature which compare the mesophase behavior of polymeric systems to that of their low molar mass analogues,[24,25] there is an absence of systematic studies aimed at the HTP's in chiral nematic monomer vs polymer systems.

In copolymeric systems based on cholesterol, the HTP has been shown to be similar to that of a low molar mass mixture,[2,20] but the nematic components in the low molar mass and polymer systems assume different chemical structures. On the other hand, a series of polysiloxanes[26] has been demonstrated to possess higher HTP values than their chemically similar low molar mass derivatives. Furthermore, it has been shown that the HTP's of the polysiloxanes approach those of low molar mass counterparts with an increasing spacer length to the nematogenic moiety.[26] These results suggest that comparative studies of HTP between low molar mass and polymeric systems are meaningful only with defined molecular structures and spacer length. Hence, in this paper, a low molar mass analogue of the nematogenic monomer based on a *p*-methoxybiphenyl benzoate core structure and those of chiral monomers containing groups derived from (*S*)-(+)-2-methoxy-2-phenylethanol, (*S*)-(−)-1-phenylethanol, and (*R*)-(−)-methyl mandelate have been synthesized and characterized. In addition, new copolymers based on (*S*)-(+)-2-methoxy-2-phenylethanol have been included. The issues of helical sense and HTP have been addressed using these new systems and previously reported copolymers containing (*S*)-(−)-1-phenylethanol and (*R*)-(−)-methyl mandelate.[27]

II. Experimental Section

All the reagents necessary for the synthesis of monomers, copolymers, and low molar mass analogues of monomers are the same as used previously[27] with the exception of (*S*)-(+)-2-methoxy-2-phenylethanol (98%, Aldrich Chemical Co.) and isobutyric acid (99+%, Aldrich Chemical Co.), which were used as received. The reaction schemes reported earlier[27–29] were followed except for the synthesis of low molar mass analogues, for which isobutyric acid instead of methacrylic acid was used. The experimental procedures and the instrumentation for characterization were all as described elsewhere.[27–29] An elemental analysis of LMMA1, which is the low molar mass analogue of the nematogenic monomer, showed C = 73.55% and H = 6.95% (Oneida Research Services, Inc.), which compared favorably to the theoretical values of C = 73.45% and H = 6.99%. The purity of all low molar mass analogues was verified with ^{1}H NMR spectroscopy and with HPLC (Hitachi, L-4200/L-6200) to be

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* To whom correspondence should be addressed.

[†] Present address: Kaiser Electronics, San Jose, CA 95134.

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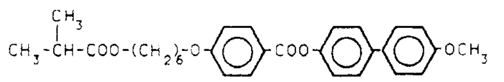
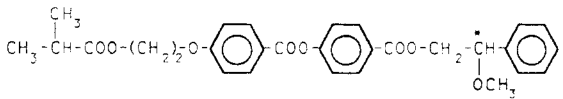
Table I
Chemical Structures and Thermal Properties of the Low Molar Mass Analogues (LMMA) Used in the Present Study

Nematogenic LMMA1



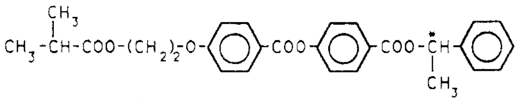
K(I) 323 K(II) 362 N 447 I (second heating scan on DSC)

Chiral LMMA2 containing (S)-(+)-2-methoxy-2-phenylethanol



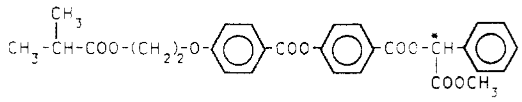
Isotropic liquid at room temperature

Chiral LMMA3 containing (S)-(-)-1-phenylethanol



Isotropic liquid at room temperature

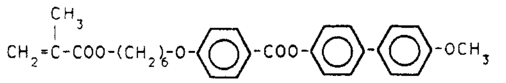
Chiral LMMA4 containing (R)-(-)-methyl mandelate



Isotropic liquid at room temperature

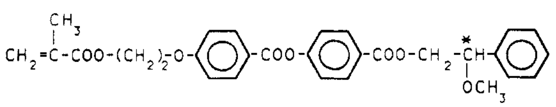
Table II
Chemical Structures and Thermal Properties of the Monomers Investigated

Nematogenic Monomer



K 357 N 451 I, Ref. 29.

Chiral Monomer containing (S)-(+)-2-methoxy-2-phenylethanol



K 357 I

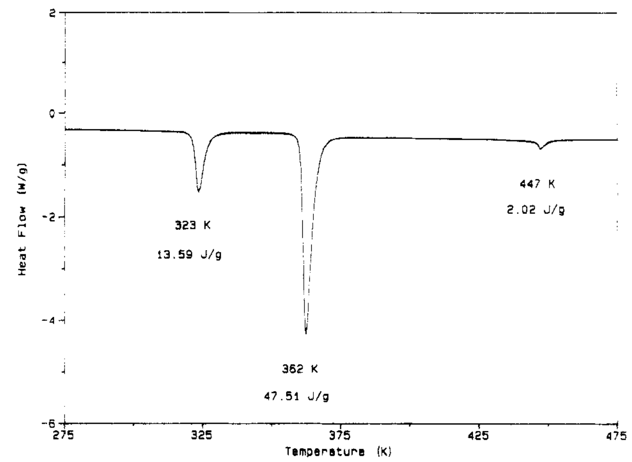
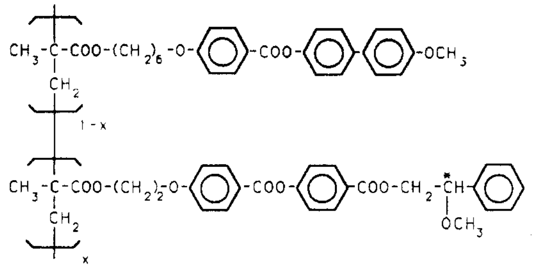
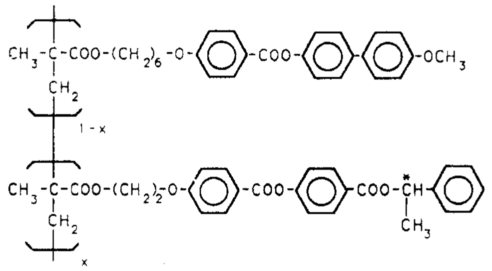


Figure 1. Second heating scan on DSC of nematogenic LMMA1.

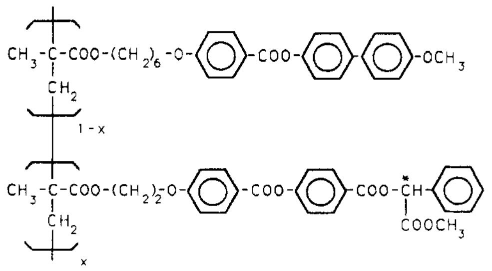
Table III
Chemical Structures of Chiral Nematic Copolymers



Copolymer 2. based on (S)-(-)-1-phenylethanol



Copolymer 3. based on (R)-(-)-methyl mandelate



better than 99%. The mole fraction of the chiral component in polymeric as well as low molar mass systems was determined from the integration of the proton signals on their respective NMR spectra. All optical elements fabricated from copolymers were consistently annealed at 95% of their respective clearing temperatures followed by quenching prior to the measurement of λ_R, the selective reflection wavelength. In the case of low molar mass mixtures, λ_R was determined using a programmable hot stage (FP52, Mettler) on a UV/vis/near-IR spectrophotometer (Lambda 9, Perkin-Elmer). Before these measurements were made, the alignment of the hot stage was checked by measuring λ_R of the copolymer sample based on (*S*)-(+)-2-methoxy-2-phenylethanol (28 mol % chiral content) to ensure that the procedure was appropriate.

III. Results and Discussion

The chemical structures and thermal properties of the new low molar mass analogues (LMMA) and monomers are given in Tables I and II, respectively. Table III shows the chemical structures of the new copolymer and the previously reported[27] copolymers 2 and 3 based on (*S*)-(−)-1-phenylethanol and (*R*)-(−)-methyl mandelate, respectively. It is evident that the chemical structures of the low molar mass analogues closely resemble the repeat units of the nematogenic and chiral components in the copolymers synthesized for this work and those reported earlier.[27] Although LMMA1 showed an endotherm at 323 K preceding the melting transition at 362 K during the second heating scan on a differential scanning calorimeter (DSC) (see Figure 1), no change in morphology or texture could be detected with hot stage polarized optical microscopy with a magnification factor of 100. This observation suggests that the endotherm at 323 K may be due to a crystalline modification. Furthermore, LMMA1 showed a broad nematic temperature range with an isotropic transition occurring at 447 K. To ascertain the chemical purity of LMMA1, elemental analysis was conducted in addition to ^{1}H NMR spectroscopy and HPLC, as described in section II.

The three low molar mass chiral analogues, LMMA2, -3, and -4, based on (*S*)-(+)-2-methoxy-2-phenylethanol, (*S*)-(−)-1-phenylethanol, and (*R*)-(−)-methyl mandelate, respectively, were found to be isotropic at room temper-

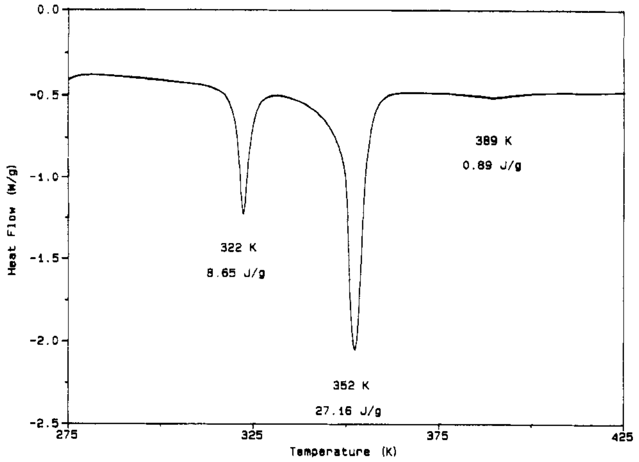


Figure 2. Second heating scan on DSC of low molar mass chiral nematic mixture with LMMA1/LMMA3 = 76/24.

Table IV
Structural, Thermal, and Optical Properties of Chiral Nematic Mixtures

mole fraction of chiral moiety x	cholesteric mesophase range (K)	λ_R (nm)	$10^4 d\lambda_R^{-1}/dx$ (nm^{-1})
LMMA1 and LMMA2 Based on (*S*)-(+)-2-Methoxy-2-phenylethanol			
0.19	352–410	997	54.8 ± 1.7
0.24	350–403	734	
0.29	348–394	634	
LMMA1 and LMMA3 Based on (*S*)-(−)-1-Phenylethanol			
0.14	355–413	851	79.2 ± 4.6
0.19	353–401	629	
0.24	352–389	558	
LMMA1 and LMMA4 Based on (*R*)-(−)-Methyl Mandelate			
0.21	354–398	1259	37.6 ± 0.4
0.24	353–388	1098	
0.30	353–379	894	

Table V
Structural, Thermal, and Optical Properties of Copolymer 1

x	T_g (K)	$T_{Ch\to I}$ (K)	λ_R (nm)	$10^4 d\lambda_R^{-1}/dx$ (nm^{-1})	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
0.20	317	489	937	56.6 ± 2.1	21.9	1.5
0.24	338	486	714		25.0	1.6
0.28	337	481	626		22.6	1.5

ature as observed under polarized optical microscopy. However, mixtures of these with LMMA1 were all found to give rise to the cholesteric mesophase beyond the crystal to cholesteric transition temperature of the mixture, as indicated by a combination of polarized optical microscopy and the DSC analysis shown in Figure 2 as an example. Complete miscibility of the chiral and nematogenic components in the mixtures occurs in the liquid state as evidenced by an absence of any residual nematic texture above the cholesteric to isotropic transition temperature, which is much lower than the nematic to isotropic transition temperature of LMMA1 for all the mixtures studied.

The structural, thermal, and optical properties of these induced cholesterics are given in Table IV. All three low molar mass systems are characterized by a decreasing trend of their cholesteric to isotropic transition temperatures with increasing chiral content. While LMMA2 was found to give rise to a right-handed cholesteric helix, both LMMA3 and LMMA4 result in a left-handed helix. In view of these results, it appears that SED and SOL observed for LMMA2 and LMMA3, respectively, are in accord with the set of empirical rules proposed by Gray et al.;[9] nevertheless, ROL observed for LMMA4 represents an exception to the rules as noted by Gray and McDonnell[9] for some chiral nematics. Deviation from this set of rules was also observed by Goodby and co-workers[30] in the case of ferroelectric smectic liquid crystals involving chiral centers with strong electronegative substituents. However, subsequent studies by Mikami and co-workers[31] on a different series of ferroelectric liquid crystals showed compliance with the empirical rules with no dependence of the helical sense on the nature of the substituents at the chiral carbon. The structural, thermal, and optical properties of copolymer 1 containing (*S*)-(+)-2-methoxy-2-phenylethanol are summarized in Table V. In contrast to the previously reported copolymers 2 and 3, which show a strong decreasing trend of the cholesteric to isotropic transition temperature with increasing chiral content, copolymer 1 is characterized by a relatively weak dependence of clearing temperature on the chiral content. Furthermore, copolymer 1 was found to give rise to a right-handed helical structure at the supramolecular level. On the basis of these findings and those reported earlier,[27] it is concluded that the helical sense observed in the copolymers is consistent with low molar mass analogues although conformity with the empirical rules is not seen in the case where methyl mandelate is involved as a chiral moiety.

The other relevant issue is the HTP defined[2] 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 monomer in a copolymer or in the mixture of low molar mass analogues. On the basis of a group contribution method,[32] we found that, for the systems under investigations, $\bar{n}$ does not vary by more than ±3%. Since the experimental uncertainty associated with the measurement of λ_R is ±5%, the slope of the λ_R^{-1} vs x at $x \to 0$ is a reasonable measure of HTP, as plotted for the low molar mass analogues and copolymers in Figures 3 and 4, respectively. Note that λ_R has been consistently measured at 95% of the clearing temperature in the case of low molar mass mixtures, while for copolymers λ_R has been measured on samples prepared by annealing at 95% of the clearing temperature followed by quenching.

It is clearly demonstrated that while the low molar mass systems based on (*S*)-(−)-1-phenylethanol and (*R*)-(−)-methyl mandelate both show HTP values (79.2×10^{-4} and 37.6×10^{-4} nm^{-1}, respectively) much lower than their corresponding copolymers (93.6×10^{-4} and 55.3×10^{-4} nm^{-1}, respectively), the HTP value of the system based on (*S*)-(+)-2-methoxy-2-phenylethanol (54.8×10^{-4} nm^{-1}) is only slightly lower than that of copolymer 1 (56.6×10^{-4} nm^{-1}). In view of the model proposed by Finkelmann et al.,[13] the higher values of HTP observed for copolymers 2 and 3 than their low molar mass analogues can be explained on the basis of a hindered rotation of the chiral pendant groups about their long molecular axes because of their linkage to the polymer backbone.[26] This observation is analogous to the role of the spacer to the nematic core for a given chiral moiety in affecting the HTP of the siloxane copolymers.[26] However, in the case of (*S*)-(+)-2-methoxy-2-phenylethanol, the effect of polymerization does not seem to have an appreciable effect on the HTP for reasons unclear to us at this point. It might be that for (*S*)-(+)-2-methoxy-2-phenylethanol the spacer is long enough to minimize the effect of polymerization on enhancing HTP.

The effect of temperature on λ_R was further studied for one chiral nematic mixture from each system with the lowest chiral content: LMMA1/LMMA2 = 81/19, LMMA1/LMMA3 = 86/14, and LMMA1/LMMA4 = 79/21.

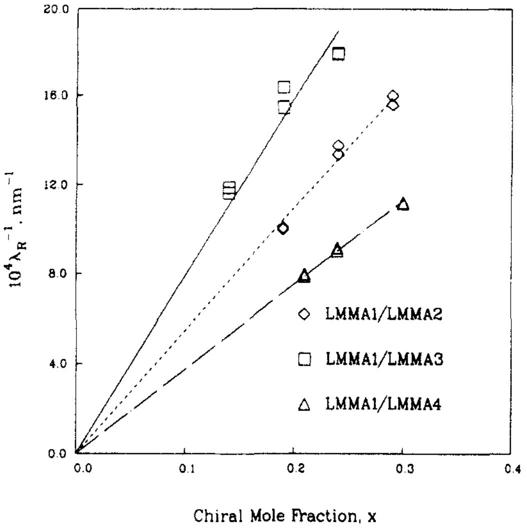


Figure 3. Linear relationship between λ_R^{-1} and x for the evaluation of HTP of low molar mass chiral nematic mixtures LMMA1/LMMA2, LMMA1/LMMA3, and LMMA1/LMMA4.

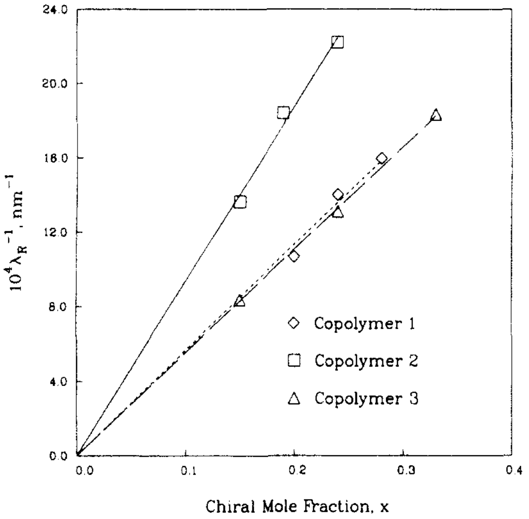


Figure 4. Linear relationship between λ_R^{-1} and x for the evaluation of HTP of chiral nematic copolymers 1, 2, and 3.

The selected systems possess the widest temperature range where the cholesteric mesophase exists, thereby permitting an investigation of the temperature dependence of λ_R. It was found that all three mixtures show increasing values of λ_R with decreasing temperature, with the systems based on (*S*)-(−)-1-phenylethanol and (*R*)-(−)-methyl mandelate exhibiting stronger temperature dependences than the one based on (*S*)-(+)-2-methoxy-2-phenylethanol. Assuming $\bar{n}$ to be only weakly dependent on temperature, which has been demonstrated in a number of low molar mass chiral nematic systems,[33] and using the relationship $\lambda_R = \bar{n}p$, we remark that the pitch length, p, increases with decreasing temperature. The absence of a smectic peak on the DSC scan and the observed linear dependence of λ_R on T^{-1} for all three systems, as shown in Figure 5, combine to preclude near-transitional effects in the framework of Keating's model.[34] In addition, the linear dependence of λ_R on T^{-1} in these systems seems to suggest the "steric" effect to be dominant over the "polar" effect in the context of the molecular statistical theory of Kimura et al.[35] incorporating dispersive and repulsive forces.

IV. Summary

On the basis of the comparative studies of the induced cholesteric mesophase formed by low molar mass analogues and copolymers, the following observations are made: (1) handedness observed in low molar mass mixtures containing (*S*)-(+)-2-methoxy-2-phenylethanol or (*S*)-(−)-1-phenylethanol complies with the set of empirical rules proposed by Gray et al., whereas the system based on (*R*)-(−)-methyl mandelate is another exception to the rules; (2) handedness in low molar mass systems is consistent with that observed in corresponding copolymer systems; (3) HTP enhancement as a result of hindered rotation imposed on the chiral pendant groups upon polymerization is observed in the systems based on (*S*)-(−)-1-phenylethanol and (*R*)-(−)-methyl mandelate but is insignificant in the system based on (*S*)-(+)-2-methoxy-2-phenylethanol; (4) all three low molar mass chiral nematic mixtures show an increasing value of λ_R with decreasing temperature, which has been interpreted in terms of Keating's model and the molecular statistical theory of Kimura et al.

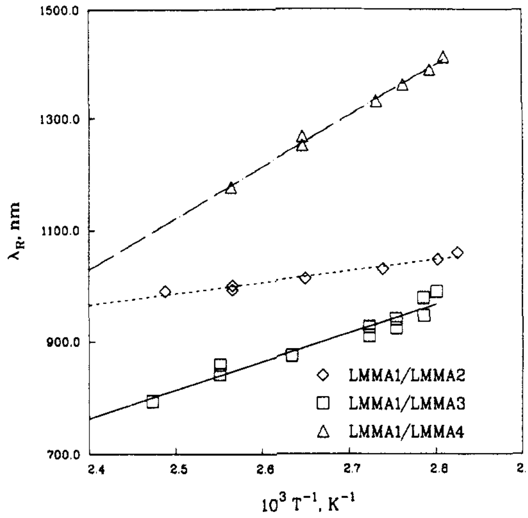


Figure 5. Linear relationship between λ_R and T^{-1} of low molar mass chiral nematic mixtures with LMMA1/LMMA2 = 81/19, LMMA1/LMMA3 = 86/14, and LMMA1/LMMA4 = 79/21.

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