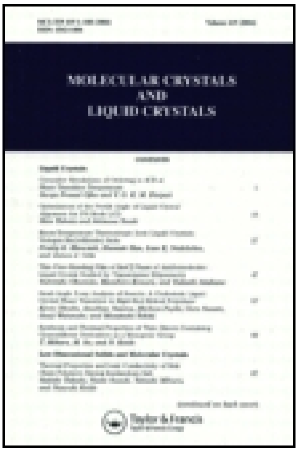

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Chiral Liquid Crystalline Polymers: Recent Trends and Perspectives in Synthesis and Electrooptical Applications

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CHIRAL LIQUID CRYSTALLINE POLYMERS: RECENT TRENDS AND PERSPECTIVES IN SYNTHESIS AND ELECTROOPTICAL APPLICATIONS

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ABSTRACT We briefly review several aspects of the syntheses and structures of chiral liquid crystalline polymers (LCPs), with emphasis on the established structure-property correlations. The current progress and future trends in their potential application in electrooptics are also outlined, with particular reference to the electrooptic effects in the smectic C* (ferroelectric) and smectic A* (electroclinic) phases of LCPs. We then present our most recent results in the synthesis and application of chiral LCPs, especially the linear electrooptic effects in chiral smectic A* and chiral nematic polymers.

Introduction

Liquid crystalline polymers (LCPs) present a unique combination of the characteristics peculiar to liquid crystals with those typical of polymers. While the former include molecular polarizability, self-assembly tendency, diversity of structures, and fast response to external electric or magnetic fields, the latter can feature variety of molecular architectures, dimensional stability, mechanical orientability, durability, ease of processability, and moldability.

Depending upon specific structural factors, essentially two types of ordering can be adopted by the mesogenic units in the mesomorphic state of LCPs, namely the orientational order such as in the nematic phase, and the orientational and positional orders such as in the smectic phases.

A preferentially chiral perturbation exerted at the molecular level or in the bulk of LC materials induces the formation of chiral nematic [1] or chiral smectic [2] supramolecular assemblies endowed with a macroscopic twist superposed on them (Figure 1). Accordingly, the nematic phase tends to twist and assemble in a helical array characterized by a prevalent screw sense of the director of each nematic plane. Similarly, the tilted smectic phases, most typically the smectic C phase, when consisting of optically active molecules, give rise to a stacking of layers with a preferential twist of the tilt director. Therefore, molecular chirality, inherently or externally established, imparts form chirality to the mesophase, and these two particular features of symmetry in liquid crystals are tightly interconnected [3].

Chirality and optical activity can be generated systematically in liquid crystals through the rational design and synthesis of new materials, and in turn the molecular chirality produced in the constituent molecules can be used in the control of the chirality of the mesophase. This consistently offers an additional valuable means of tuning the liquid crystal behavior and addressing specific responses of chiral LCPs in special applications, namely in electrooptics.

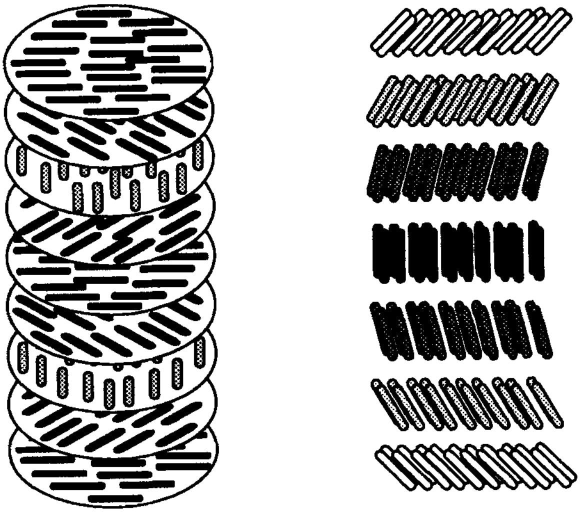


FIGURE 1. Schematic representation of the chiral nematic (left) and chiral smectic C* (right) mesophases.

Synthesis of chiral LCPs

According to the particular location of the mesogenic (rod-like or disc-like) components in the macromolecule, LCPs have conventionally been divided into the two broad categories of main-chain and side-chain polymers, but new combined polymers have also been developed. While in the first two polymer architectures the mesogens are either incorporated as primary constituents of the polymer backbone or appended to it as substituents in the side chains, in the last family they are present simultaneously in both the main and the side chains of LCPs. Crosslinked, elastomeric or thermosetting, LCP materials are also attracting ever increasing attention especially for their characteristics of mechanical orientability and thermal and dimensional stability (Figure 2).

There exist basically four methods to introduce chirality into LCPs [4] by:

i) polymerization of intrinsically chiral mesogens;
ii) polymerization of chirally perturbed mesogens;
iii) chemical modification of (liquid crystalline) polymers;
iv) mixing LCPs with chiral dopants.

Cholesterol containing polymers belong to the first category of chiral LCPs [5] and, in a wider sense, other available examples are the cellulose derivatives [6] and polypeptides [7]. Mixtures of polymers with chiral dopants have been more rarely investigated [8], their use being quite often limited by the difficulty of overcoming miscibility or compatibility problems between the components, which in turn resulted in poorly defined phase diagrams. However, most recent developments of this strategy have shown that mixing an optically active dopant with a nematic elastomer resulted in a polymeric material endowed with a noteworthy piezoelectric response [9]. According to the third method above, the polymerization of a chirally perturbed mesogen and the copolymerization of an achiral mesogenic monomer with an optically active, not necessarily mesogenic comonomer, have been most commonly exploited for the synthesis of chiral LCPs [10].

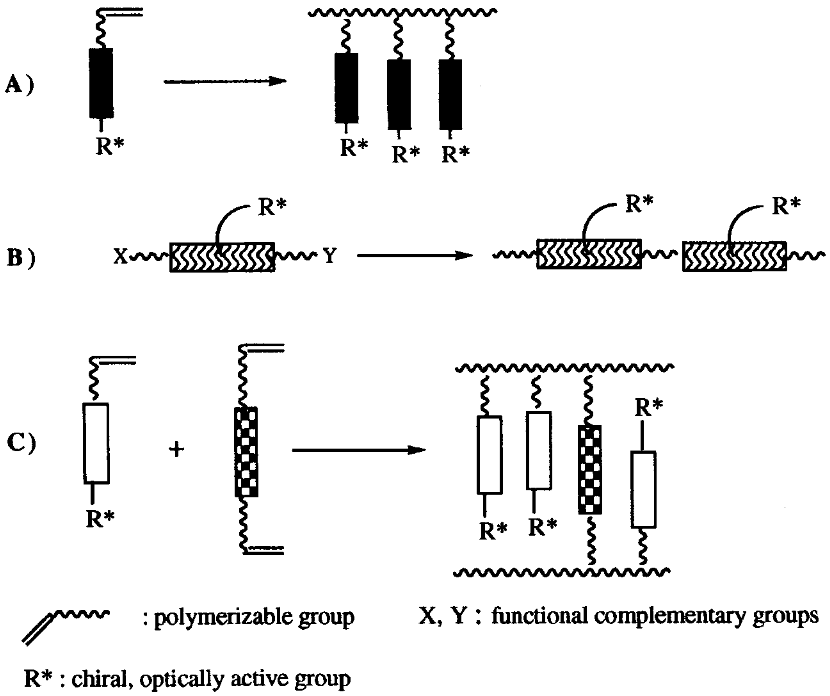
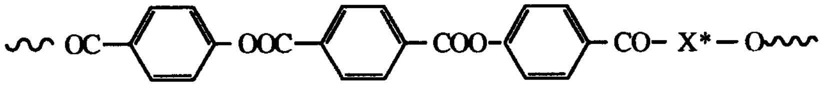


FIGURE 2. Schematic representation of example syntheses of chiral LCPs: (A) side chain, (B) main chain, and (C) crosslinked polymers.

In a complementary approach, the polymerization of mesogenic diacids with a variety of chiral, flexible diols for the preparation of structurally ordered LC polyesters based on the 4,4'-terephthaloyldioxydibenzoyl mesogen has been investigated in a systematic way [11-15]. In this context, the influence on the mesomorphic properties of polymer structural parameters was elucidated such as the length and nature, substituent structure, structural isomerism, and enantiomeric excess, e.e., of the chiral spacer segment. It is important to recognize that in polyesters **1** and **2** of this class the gross mesophase behavior did not depend substantially on the e.e. of the chiral alkylene spacer over the entire range 0-100%.



X*	
$-CH^*(CH_3)CH_2CH_2-$	**1**
$-CH_2CH^*(CH_3)CH^*(CH_3)CH_2-$	**2**

In contrast, fine details of the mesophase structure and physical properties were affected by varying e.e. [13] and this suggests that stereochemical factors should also be taken into serious account when designing chiral LCPs for some special application. Very recently, the question of chiral molecular recognition and discrimination in chiral LCPs has been arisen for polymers containing different stereogenic centers (R and S enantiomers) [16] for which, in principle, enhanced effects should be expected with respect to low molar mass systems [17]. The absence of chiral recognition was ascribed to the irregular microstructure of the linear polymers.

Finally, the chemical modification of preformed polymers has been explored in a few cases by the selective modification of not mesomorphic chiral polymers [18] or by the enantioselective modification of suitable prochiral mesomorphic polymers [19]. In contrast, polymer analog reactions are very commonly used for the synthesis of chiral LCPs, for instance by grafting chiral mesogenic olefins or vinyl ethers onto the highly versatile poly(hydrogenmethylsiloxane) parent polymers [5,20].

There is, therefore, a vast potential for the synthesis of specifically designed polymers whose properties can be tuned on a structural basis and successful applications of these synthetic efforts have led to the development of new polymeric materials exhibiting greatly differentiated physical and mechanical properties. Conversely, this has generated further stimulus for both improving the understanding of structure-property relationships and assessing specific aspects of the complex physical character of LCPs in view of their use in novel technologies. There is thereby an enlarged scope for the use of chiral LCPs, along with the more conventional low molar mass analogs, and a number of potential applications have been explored to date.

Most recent and extensively investigated effects fall, broadly speaking, into the class of electrooptic effects. Chiral smectic polymers are attracting special attention, under academic and industrial standpoints, for their associated ferroelectric and nonlinear optical properties (smectic C*) or electroclinic properties (smectic A*). We have also found a linear electrooptic effect in chiral nematic (long pitch) polymers.

Chiral smectic C* LCPs

Alomst twenty years ago, it was shown [21] that in the smectic C* phase, which lacks mirror symmetry, the tilting of the molecules away from the smectic layer normal induces a bias of the rotation of the molecules around their long molecular axis. This leads to a spontaneous polarization in each individual layer, if the molecules possess a transverse dipole moment parallel to the layer planes. However, due to the helical superstructure, the tilt direction is rotated about the normal to the layer planes, and consequently the layer polarization is averaged to zero. If the helix is completely unwound, for instance by surface action, the layer polarizations will point in the same direction and hence the phase becomes *ferroelectric* with a net bulk spontaneous polarization, Ps, (Figure 3).

In surface-stabilized ferroelectric liquid crystal displays an electrooptic effect was first implemented [22] with a fast switching between the two equally stable orientations of the molecules when the polarity of the applied electric field was reversed (Figure 4). After that bistability in this so-called bookshelf geometry was realized, interest in ferroelectric liquid crystals increased enormously and active research on the suitability of smectic C* polymers as ferroelectric candidates was also initiated [23]. It may be expected, in fact, that in these chiral materials the ferroelectric structure and properties will be frozen, thus making it possible to develop robust films using various birefringence or absorption based fast electrooptic effects wih additional memory properties.

Initially, synthetic efforts were devoted primarily to optimizing the spontaneous polarization in smectic C* LCPs in order to define structure-property correlations for this

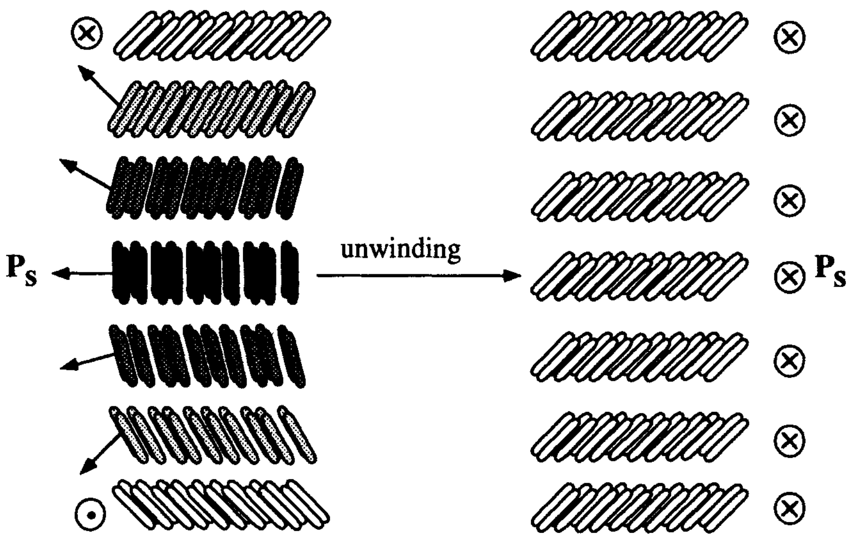


FIGURE 3. Structure of the helical (left) and unwound (right) smectic C* phase.

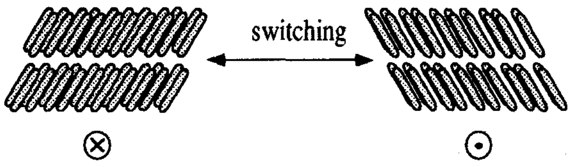
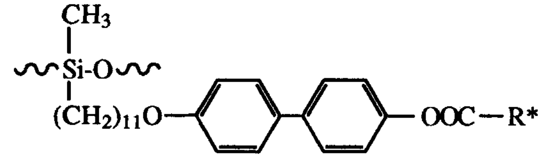
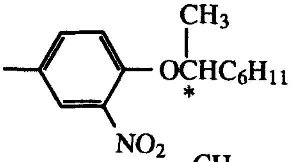
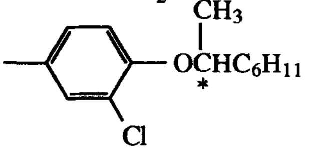
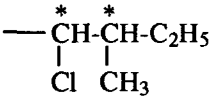


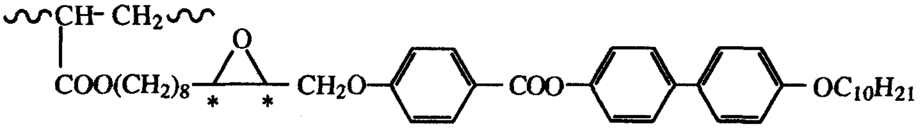
FIGURE 4. Switching of ferroelectric liquid crystals: spontaneous polarization inward (left) and outward (right).

new class of materials [24-32]. It was argued that the spontaneous polarization should be increased in order to reduce the response time, τ, in electrooptic devices. A number of ferroelectric polysiloxanes (**3-5**) with high values of Ps have been prepared by a combination of different chiral terminal groups and bulky highly polar lateral substituents [32]. It has been proposed that in these polymers the bulky lateral substituent can strongly bias the rotation of the biphenyl mesogen around its long axis. This would lead to a strong preference for one orientation, thus substantially enhancing the time-dependent spontaneous polarization. The reported value of Ps = 420 nC/cm^2 for polymer **3** is probably the highest value so far achieved with LCPs. However, it was found that strong lateral dipole moments in the mesogens, leading to high Ps, also increase the viscosity and consequently τ.



R*	Ps (nC/cm^2)	
	420	**3**
	120	**4**
 $-\overset{*}{C}H(Cl)-\overset{*}{C}H(CH_3)-C_2H_5$	130	**5**

Therefore, it is necessary to reduce both the viscosity and the spontaneous polarization in order to obtain short switching times. This can be achieved by making mixtures of host smectic C liquid crystals with optically active dopants that have a large polarization but are not necessarily liquid crystals [33,34]. These guest molecules are only present in the mixture in low concentrations, usually of the order of 10%. Analogous to most low molar mass ferroelectric liquid crystal mixtures, one optically active phenylpyrimidine dopant was used to induce a spontaneous polarization in a racemic smectic C polyacrylate [35]. Furthermore, it has been shown that in polymer **6** the phenomenon of sign reversal of Ps can occur with varying temperature at the inversion temperature in the smectic C* phase [36]. This sign reversal of Ps is attributed to a temperature dependent equilibrium between different conformers of the chiral molecules, which have opposite signs of Ps [37]. In polyacrylate **6**, the chiral oxirane ring in the spacer segment could enforce conformations that compensate the two opposite tilt directions of the molecules at the inversion temperature.



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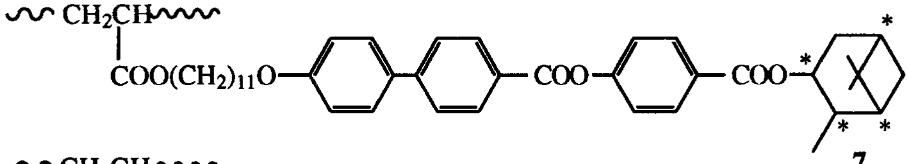
While typical examples of switching times are in the order of a few milliseconds [36,38,39], examples of polysiloxanes, homopolymers and copolymers, have shown ferroelectric switching times as fast as 150 μs at the smectic C*-smectic A* transition

[30]. Therefore, optimal values of τ of ferroelectric LCPs are comparable to those of low molar mass LCs and there is a promise that they may compete with conventional ferroelectrics in large, flexible displays with high information content.

More recently, tristable ferroelectric polymers **7-9** have also been described [40-42]:



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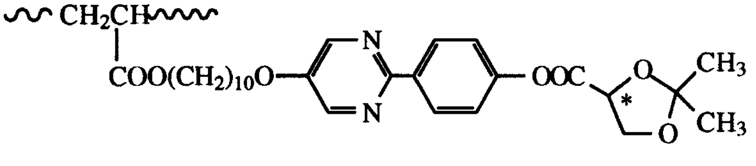

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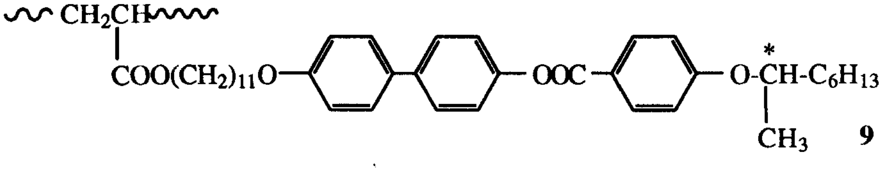

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The existence of a third switching state in these polymers has been attributed to a new antiferroelectric molecular ordering [43]. In the antiferroelectric smectic C* phase the molecules, and accordingly the polarization vectors, in subsequent layers point in the opposite directions, thereby cancelling each other and resulting in an almost zero Ps (Figure 5).

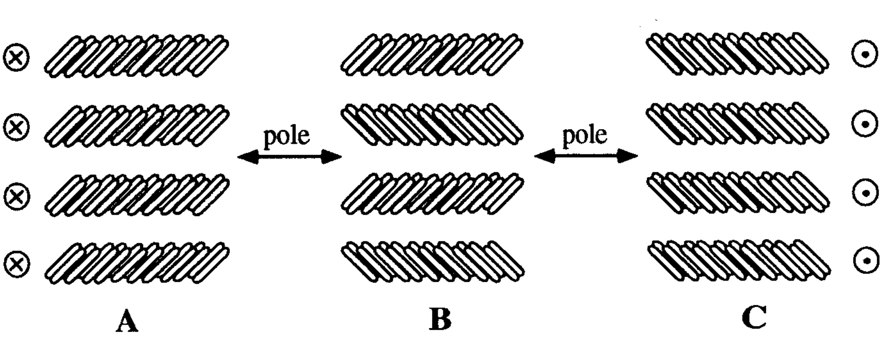
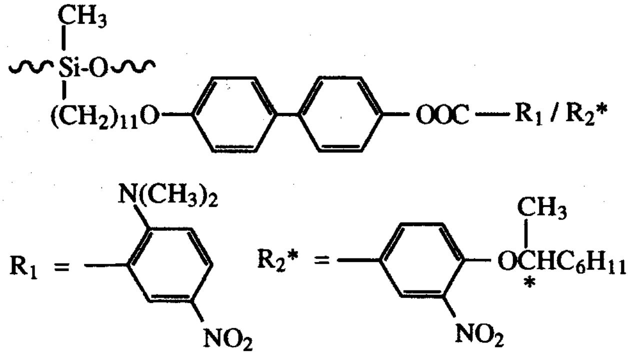


FIGURE 5. Ferroelectric (A or C)-antiferroelectric (B) switching.

In a way, the proposed structure has a kind of pitch of only two layers, superposed on which is the normal, weak helix. There is a sharp field threshold for swithching from the antiferroelectric to the ferroelectric phase, which accordingly would appear to be of great utility in display applications that rely on the multiplexing of a large number of pixels in order to operate. The actual antiferroelectric state of chiral LCPs needs to be better established, but it is possible to anticipate that the conformational interactions between the side chain groups and the main chain can lead to quite peculiar electrooptic responses. We may expect, in fact, that while mesogens latch and switch very quickly, the polymer backbone will respond by undergoing various possible, not easily predictable motions.

A material potentially able to exhibit significant second-order *nonlinear optical* (NLO) responses must be characterized by a noncentrosymmetric structure. Electric field poling of polymers containing a dipolar chromophore originating large values of the second-order susceptibility, $\chi^{(2)}$, is a common method to introduce a polar axis into the medium reducing the free orientational averaging of molecular dipoles [44]. This induced polarity can be locked-in by cooling the polymer below its glass transition, and in turn the enhanced molecular alignment can increase quite substantially the efficiency of NLO processes, such as second harmonic generation. Different polymer compositions have been realized based on similar concepts [45-47]. There is no symmetry restriction for third-order NLO processes which arise from the nonlinearity in the polarization response of all dielectric media. The π-electrons in conjugated polymers contribute much more efficiently along the chain direction than perpendicular to it. Therefore, uniaxial alignment associated with the liquid crystalline director of main-chain PLCs can result in enhanced third-order susceptibilities, $\chi^{(3)}$ [48].

An alternative approach to develop NLO PLCs might be to introduce chirality and the other structural requirements of the ferroelectric smectic C* phase into a polymeric structure containing chromophores capable of giving rise to a nonlinear response. This intrinsically noncentrosymmetric structure should be able to originate large second-order responses without the necessity of poling in the strong electric fields required with conventional NLO organic materials. In this connection, it is essential to design and synthesize LCPs incorporating specific functions to fulfil the above, sometimes conflicting, demands. However, the dye molecules usually employed do not appear best suited to enhance significantly the macroscopic $\chi^{(2)}$ values, in that their maximum molecular hyperpolarizability is typically oriented parallel to the long molecular axis, whereas the macroscopic polar axis of the smectic C* phase is oriented parallel to the smectic layers.



10

New dipolar ferroelectric liquid crystals should be designed, therefore, such as to possess an enhanced hyperpolarizability component perpendicular to the long molecular axis [49,50]. Ferroelectric LC copolymers **10** containing dipolar and chiral mesogens along with dye molecules with an appreciable hyperpolarizability component perpendicular to their long axis indeed were effective at second harmonic generation of the 1064 nm Nd:YAG fundamental, but still exhibited rather strong light scattering probably due to poor macroscopic alignment [27]. This appears to be a major drawback in using LCPs in NLO applications for which a perfect polar, not scattering monodomain must be realized. Furthermore, most NLO chromophores have strong absorbance in the visible range of the spectrum, as a consequence of the extended electronic conjugation of their molecular structure. This would lead to the second harmonic radiation being absorbed by the material. Accordingly, new nonresonant dye mesogens should be made available with sufficiently low extinction coefficient below ≈500 nm.

In another approach to the synthesis of LCPs with an electric dipole closely coupled to the chiral center and characterized by negligible UV absorption in the spectral region above 300-350 nm, we have synthesized [51] polymers incorporating chiral sulfoxide moieties in the terminal tails of side chain mesogens of polyacrylates. Optically active **12-n** were prepared by the asymmetric oxidation of the corresponding prochiral sulfide-containing polyacrylates **11-n** by using the chiral oxidant (-)-(*S*,*S*)-3-(2-chloro-5-nitrophenyl)-2-(α-2-oxo-10-bornylsulfonyl)-oxaziridine (**13**) (Figure 6).

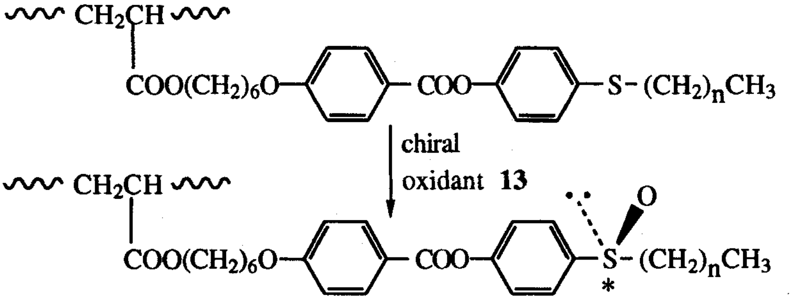


FIGURE 6. Schematic of the enantioselective oxidation of prochiral polymers **11-n** to chiral, optically active polymers **12-n**.

The enantioselective reaction proceeded with appreciable chiral discrimination, and a moderate degree of asymmetric induction (≈25%) was evaluated. The first member in this class **12-0** (n = 0) did not show LC properties. The lower homologues presented one chiral nematic mesophase, whereas the higher homologues (n = 5,7, and 9) formed disordered bilayer structures (smectic A* or C*) [52]. Therefore, by adjusting the length of the alkyl sulfide substituent in parent polymers **11-n**, it is possible to stabilize either chiral nematic or chiral smectic mesophases in modified polymers **12-n**, the cross-over point being at intermediate values of n = 5 or 6 (Figure 7). The polymers exhibited new linear electrooptic effects in their chiral nematic mesophase (see below). It will also be relevant to investigate the general electrooptic properties of the polymers incorporating optically pure chiral substituents as prepared by, e.g., enzymatic synthesis.

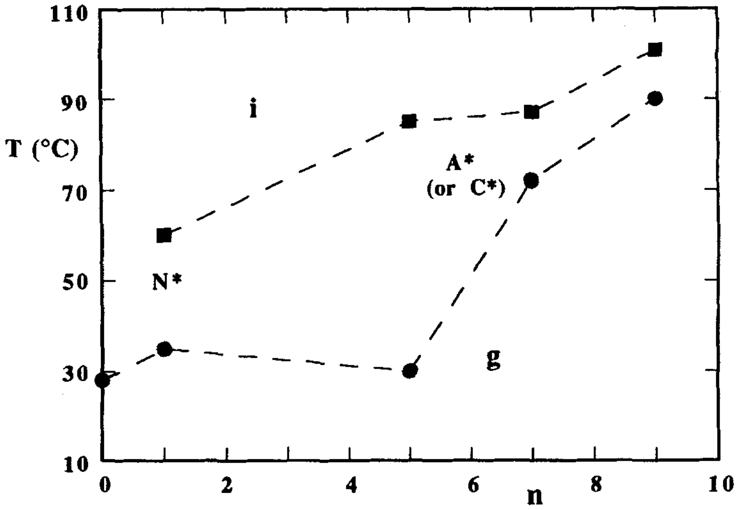
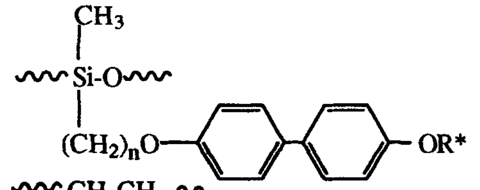


FIGURE 7. Phase diagram for polyacrylates **12-n** as a function of the number, n, of methylene groups in the terminal sulfide substituent.

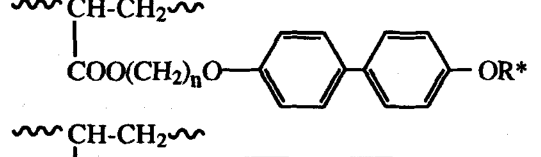
Chiral smectic A* LCPs

The *electroclinic* effect is an induced molecular tilt in the chiral orthogonal smectic phases, such as the smectic A* phase, when an electric field is applied along the smectic layers [53], the smectic layers being perpendicular to the confining substrates in a bookshelf geometry. The induced molecular tilt is a linear function of the field and results in a macroscopic induced polarization, Pi. The main features of the effect are the linear electrooptic response and a fast, sub-microsecond, switching time [54].

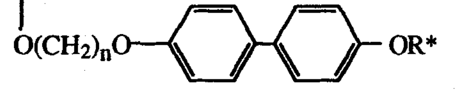
In order to elucidate the role of different structural parameters on the incidence of the chiral smectic A* phase extending over broad and accessible ranges of temperature we are examining systematically [20,55,56] different chiral LCP compositions, such as **14-16**.



14-n



15-n



16-n

R*
2-methylbutyl
1-methylheptyl
2-chloro-3-methylbutanoyl
2-chloro-3-methylpentanoyl

Polyacrylates **15-n** were characterized by a very specific tendency to give rise to the smectic A* phase, even in polymorphic forms (A_1*, A_2*, A_d*) [56]. In fact, lengthening of the spacer resulted in the evolution from a bilayer A_2* structure ($n < 7$) to a monolayer A_1* structure ($n > 7$), a partially interdigitated A_d* mesophase occurring as an intermediate situation at $n = 7$ (Figure 8). Longer spacers permitted an easier organization of the mesogenic units in a fully interdigitated structure, and it is possible to outline general guidelines for the synthesis of chiral polymers of this kind. Due to the different extent of interdigitation or overlap of the aromatic units within the smectic layers (Figure 9), we anticipate that rather different electronic properties and luminescent behaviors should characterize these polymers and have started time-resolved measurements of the fluorescence emission (monomer and excimer) of the polymers in the A* polymorphs. Furthermore, thanks to the presence of a preferentially chiral substituent bound to the mesogenic core, circular dichroism and ultraviolet absorption measurements carried out in the different smectic phases should be able to further substantiate the structural features of the smectic A* polymorphs.

In polyacrylate **17** an electroclinic type of switching was detected in the A* phase on applying an electric field [57]. The observed induced tilt angle, θ, was strongly temperature dependent as shown in Figure 10. At the transition to the isotropic phase, θ had a nonzero value, then it decreased with decreasing temperature, approaching its maximum value just above the transition temperature to the semicrystalline phase. A residual electroclinic type of electrooptic switching was also observed in the semicrystalline phase, when an electric field was applied. The apparent induced molecular tilt was much smaller ($\theta < 0.1°$) than in the A* phase (Figure 10), but the linear effect could nonetheless be detected even 50°C below the transition to that phase. The response followed the shape of the applied field with no visible threshold.

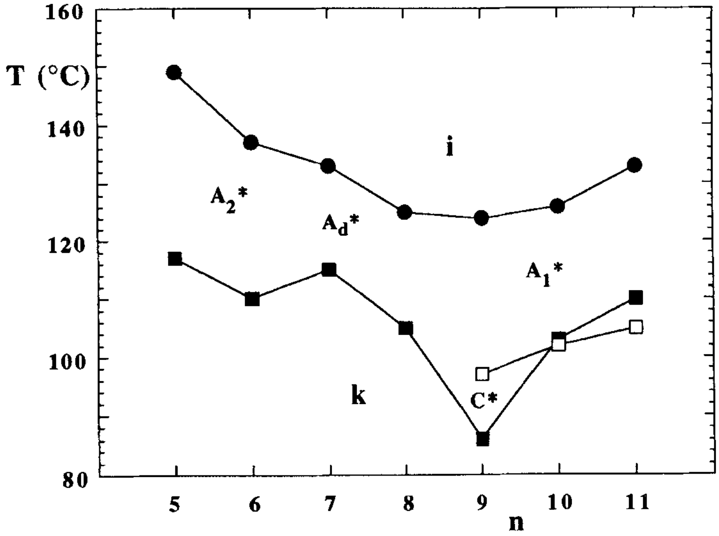
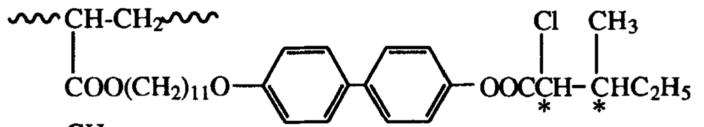


FIGURE 8. Phase diagram for polyacrylates **15-n** as a function of the number, n, of methylene groups in the flexible spacer.



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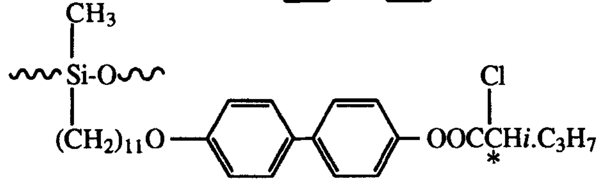

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The existence of an electroclinic effect in the semicrystalline phase of the chiral polyacrylate **17** clearly indicates that the side chain mesogenic groups still possess a substantial degree of motional freedom. The linear increase in induced tilt upon increasing the applied electric field in both A* and semicrystalline phases is further illustrated in Figure 11. In the A* phase the bare electrooptic response time, τ, was strongly temperature dependent (Figure 12) with a clear transitional behavior. At the transition to the semicrystalline phase, τ was almost two orders of magnitude larger than at the transition to the isotropic phase, but in the semicrystalline phase the detected response time was very short ($\tau = 1\ \mu s$).

The simplest expressions for θ and τ are [58]:

$$\theta = \frac{\mu E}{\alpha (T - T_c)} \qquad \tau = \frac{\gamma_\theta}{\alpha (T - T_c)} \qquad (1)$$

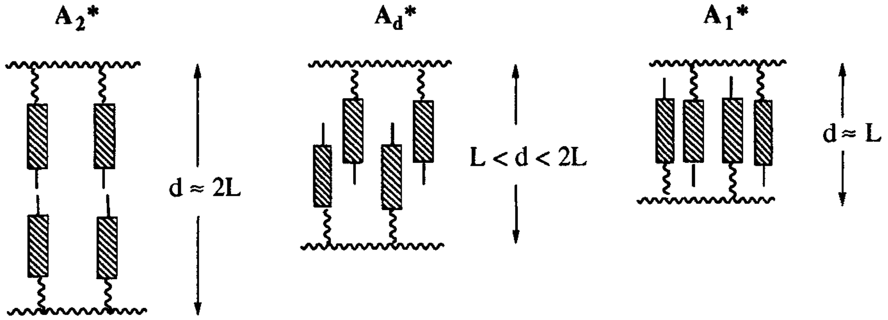


FIGURE 9. Schematic representation of different smectic A polymorhps in polyacrylates **15-n**.

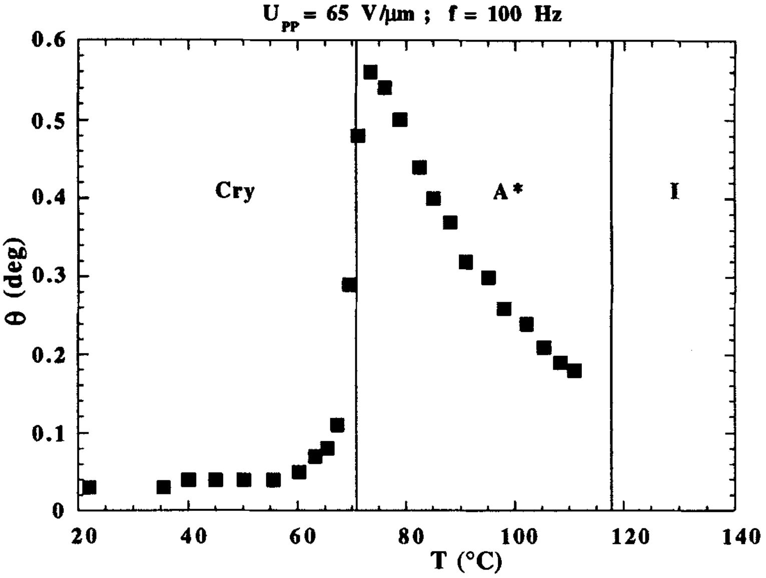


FIGURE 10. Trend of the induced tilt angle, θ, with temperature for polyacrylate **17** in the semicrystalline and smectic A* phases.

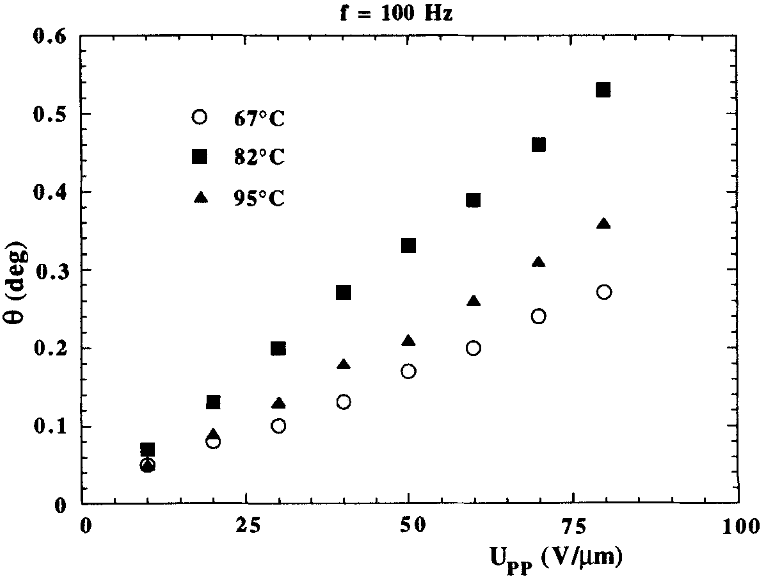


FIGURE 11. Dependence of the induced tilt angle, θ, with applied electric field, U_{PP}, for polyacrylate **17** at different temperatures in the semicrystalline and smectic A* phases.

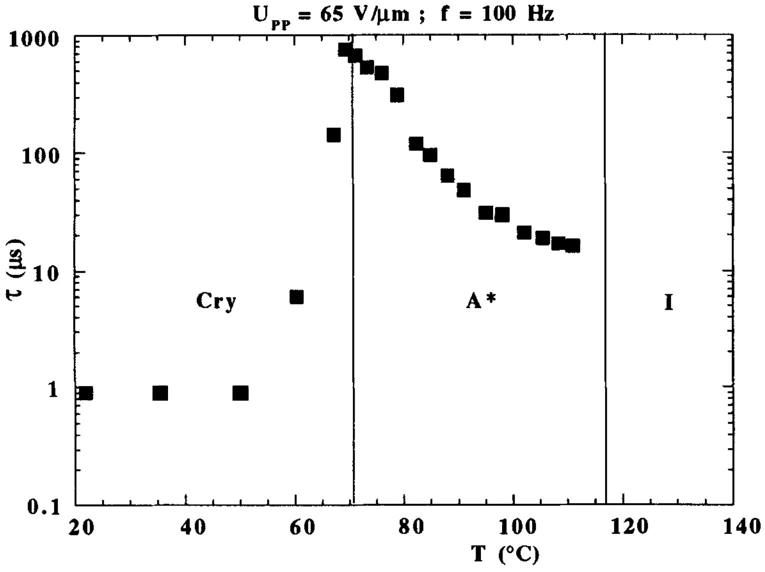


FIGURE 12. Trend of the response time, τ, with temperature for polyacrylate **17** in the semicrystalline and smectic A* phases.

In eq.1, μ (so-called structure coefficient) is the ratio of induced polarization density to induced tilt, γ_θ is the soft mode viscosity, and $\alpha(T-T_C)$ is the first coefficient, a, in the classic Landau expansion of the free energy as a function of induced tilt angle, T_C being the smectic A*-smectic C* transition temperature [58]. Both θ and τ can be expected to vary in a smooth way with temperature, μ being essentially dependent only on the molecular conformation and packing and γ_θ being expected to have a behavior typical of an activated Arrhenius process. By applying these arguments to polymer **17**, one should be able to renormalize the electrooptic response by tracing the time for unit angle response, τ/θ, thereby getting rid of the pretransitional divergent behavior. In contrast, the temperature dependence of τ/θ exhibited a stronly divergent behavior (Figure 13). This anomaly was attributed [57] to the predominant effect of a critical behavior with temperature of γ_θ at the smectic A*-semicrystalline phase transition (Figure 14). More systematic investigations are required to ascertain whether the critical behavior in γ_θ may have a more general incidence in low molar mass [59] and polymer A* liquid crystals.

A remarkable increase in the induced tilt (θ ≈ 25° at the smectic A*-smectic C*transition) was detected in the chiral LC polysiloxane **18** which still exhibited a response time in the μs regime [60]. It may be concluded, therefore, that optimized polymer structures will eventually lead to significant improvements of both θ and τ of the electroclinic effect of PLCs. While smectic C* LCPs evidently undergo several switching processes, including the ferroelectric (Goldstone) mode and the electroclinic (soft) mode [36,61], very few other examples of electroclinic A* LCPs are known [30,62].

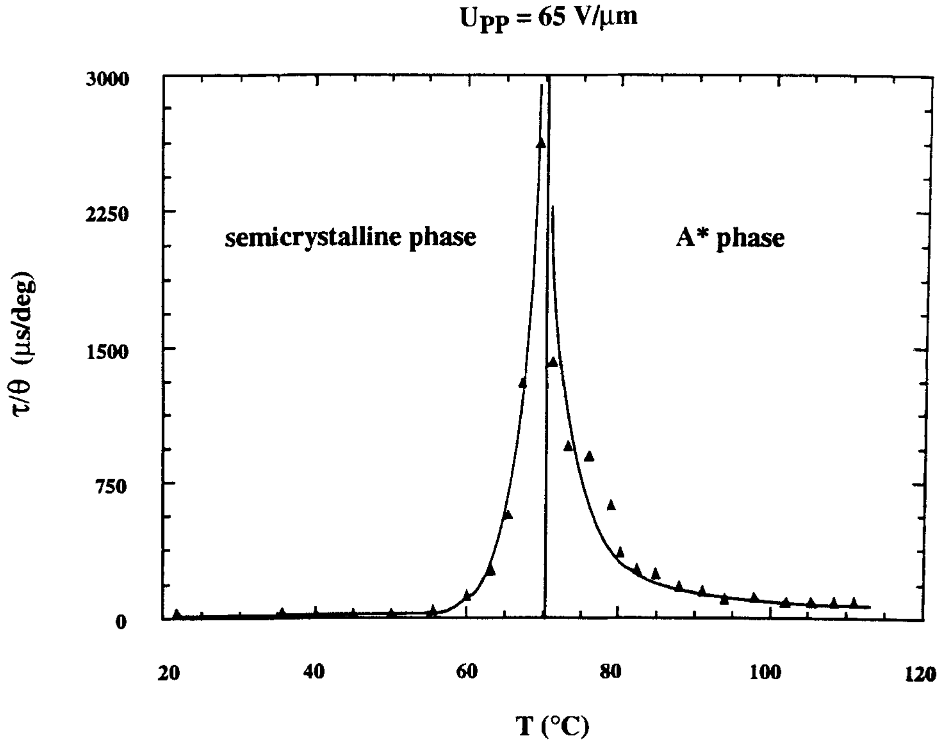
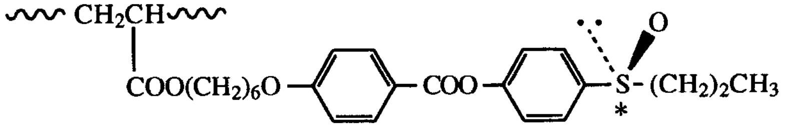


FIGURE 13. Trend of the unit tilt response time, τ/θ, with temperature for polyacrylate **17** in the semicrystalline and smectic A* phases.

The scope and applicability of this new class of polymers are still to be fully addressed, but it is possible to envision that such materials can find useful applications wherever speed or grey scale is the primary requirement and no memory is necessary. Typical areas should be those concerned with optical switching and modulating devices, as well as optical image and signal processing systems.

Chiral nematic LCPs

Most recent advances are concerned with both structure and properties of very different molecular architectures of chiral LCPs. We are exploring new electrooptic effects in the chiral nematic (N*) phase of LCPs such as **12-2**.



12-2

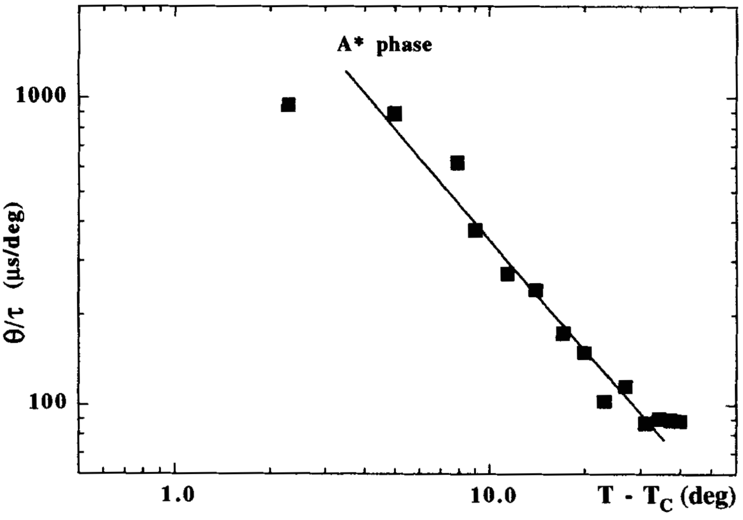


FIGURE 14. Log-log plot of unit tilt response time, τ/θ, versus reduced temperature for polyacrylate **17** at T>T$_C$.

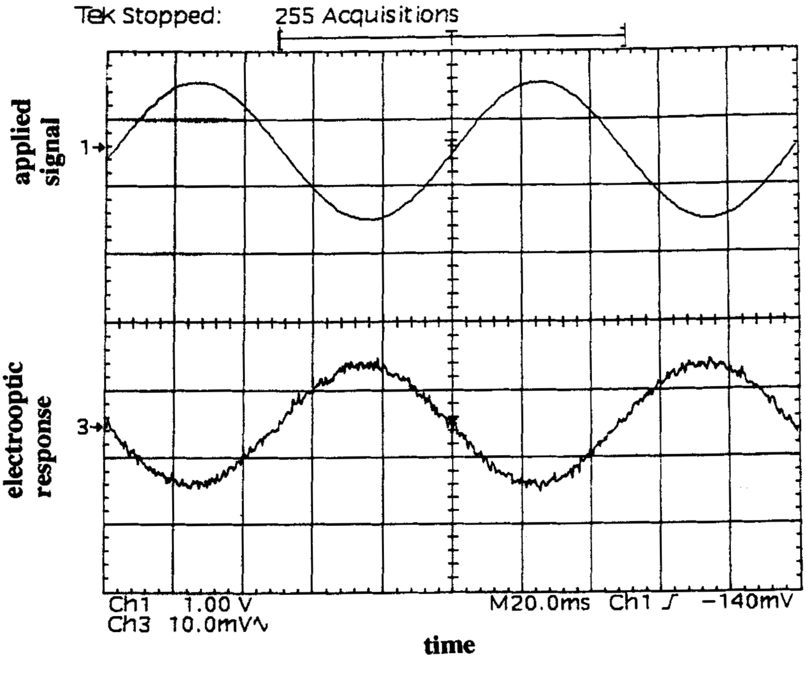


FIGURE 15. Electrooptic response as a function of time for polyacrylate **12-2** in the N* phase at 57°C (Upp = 100 V/μm; f = 10 Hz).

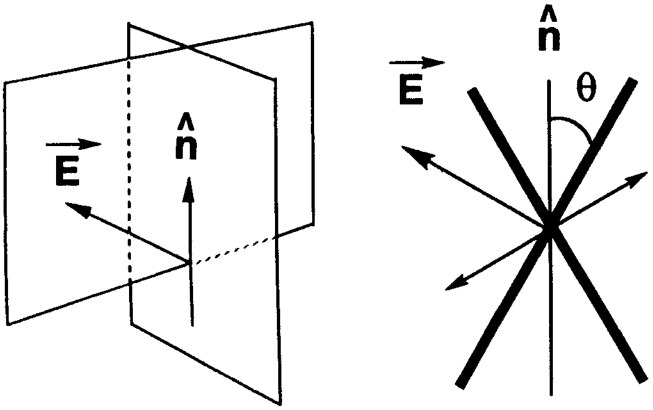


FIGURE 16. Electrically induced tilt as a consequence of loss of mirror plane **n-E**, under preservation of the two-fold rotation axis along **E** (**n** is the molecular director in the field free case) (after [63]).

In this polymer a linear electroclinic-like response has been recorded starting from above the glass transition temperature up to the chiral nematic-isotropic transition temperature (Figure 15). The induced tilt was very small (≈ 0.1°) and the switching time was relatively long (≈ 2 ms).

The linear electrooptic effect described has its origin in the subtle symmetry difference between the N and N* phases [63], which is the same as that between the A and A* phases, or the C and the C* phases. In the uniaxial N and A phases, the molecules rotate rather freely and, specifically, without any rotational bias around the **n** direction in both cases. This unbiased rotation also exists in the N* and A* phases. On applying an electric field **E** perpendicular to **n**, any lateral dipole of the molecule will tend to orient itself along the field. Hence the rotational motion will be biased and a polarization will be induced along the field direction. However, in achiral systems the plane containing **n** and **E** is a mirror plane, which in contrast is not the case for a chiral molecule. In the N* and A* phases only the two-fold rotation axis along the **E** direction is left (Figure 16). Following the absence of mirror symmetry around the **n-E** plane, if the molecule tilts out, even very slightly, clockwise or counter-clockwise, around the two-fold axis, these two positions will have no longer the same energy and the lower energy direction will be preferred. Thus the molecules will swing clockwise or counter-clockwise. Which direction will be chosen in any specific case is a molecular property and cannot be deduced by symmetry arguments [63]. However, the tilt direction will be reversed on reversing the direction of the applied electric field.

In cholesterics, the observation of an electrooptic effect linear in the applied electric field might have several different origins, including flexoelectricty [64]. It might further be associated with conductive currents in the cell, or with surface induced polar ordering. Thus, the finding of a linear response has to be interpreted with caution. Stronger cases for a more general occurrence of these new peculiar phenomena in liquid crystals should probably be required [63,65], but it is quite obvious that the specific investigation of their defect characteristics as well as elastic, electric and optical properties would greatly expand the scope for applications of chiral LCPs. Furthermore, we should expect that the increased coupling of the mesogen characteristics with the polymer characteristics could impart unique properties to chiral LCPs unprecedented by conventional low molar mass liquid crystals.

Conclusions

Today, the synthetic efforts from numerous research groups have succeeded in developing a great variety of chiral liquid crystal polymer architectures with distinct physical properties. Reliable structure-property relationships have been established for these polymers, which in turn will help address future syntheses of specifically designed structures. At the same time, the scope for application of these materials already appears wide and is continuously expanding, major attention being paid to the high-tech field of electrooptics [66]. Some potential applications of chiral liquid crystalline polymers are summarized in Table 1, as a further proof of the many interesting and novel opportunities for chiral liquid crystalline polymers.

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TABLE 1. Example potential applications of chiral LCPs.

CHIRAL NEMATICS	CHIRAL SMECTICS
Passive components	Orthogonal phases
notch filters	optical switchers
reflective color filters	modulators
polarizers	image elaborators
Active components	Tilted phases
scattering displays	high information displays
digital thermometers	transducers
thermographical tools	piezoelectric & pyroelectric sensors
piezoelectric transducers	nonlinear optical devices
holographic elements	

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