Glassy Liquid Crystals for Tunable Reflective Coloration

Amorphous Molecular Glasses

Glasses have been in existence for thousands of years, and yet they still represent one of the frontiers in materials science today.[1] They are traditionally classified as amorphous solids exhibiting isotropic properties. Cooled at a sufficiently rapid rate, all liquids should bypass crystallization to form glass. It is well known that liquid viscosity increases exponentially with decreasing temperature. Phenomenologically, the glass transition temperature T_g is defined on the basis of viscosity reaching a value of 10^{13} poise.[2] Despite intensive efforts over several decades, understanding of molecular processes accompanying glass transition has remained largely qualitative.[1,2]

Glassy films are characterized by their superior optical quality over a large area with no grain boundaries and, therefore, are ideally suited for electronics, optics, photonics, and optoelectronics.[3] Glass formation is ubiquitous among polymeric materials. To take advantage of the ease of film processing due to low melt viscosity and the feasibility of vacuum deposition, considerable efforts have been devoted in recent years to developing low-molar-mass organic materials. Existing amorphous molecular glasses can be categorized as follows: (a) bulky, odd-shaped or twin molecules;[4–6] (b) starburst molecules and dendrimers;[7–9] (c) spiro-linked molecules;[10–12] and (d) tetrahedrally configured molecules.[13] In general, an elevated T_g relative to the application temperature is desired for stability against recrystallization. Representative structures are presented in Fig. 93.42, where *G x*°C *I* expresses a T_g at *x*°C.

Glassy Liquid Crystals

It is arguable that glasses are not necessarily amorphous or isotropic. In principle, mesomorphic organic glasses can be realized by vitrifying liquid crystals through thermal quenching. Liquid crystals are a class of self-organizing fluids characterized by a uniaxial, lamellar, helical, or columnar arrangement in nematic, smectic, cholesteric, and discotic liquid crystalline order,[14] respectively, as depicted in Fig. 93.43.

Each type of liquid crystal has found its respective niche in optics, photonics, or optoelectronics. With these molecular arrangements frozen in the solid state, glassy liquid crystals (GLC's) represent a novel material class that combines properties intrinsic to liquid crystals with those common to polymers, such as glass transition and film- and fiber-forming abilities. The preparation of defect-free GLC films requires

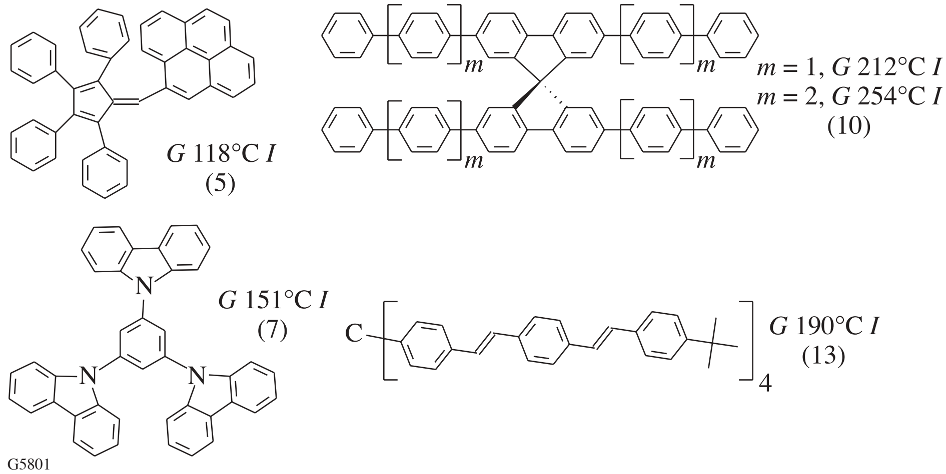


Figure 93.42
Representative amorphous molecular glasses.

slow cooling from mesomorphic melts without encountering crystallization, a challenge to thermal quenching as a conventional means to vitrification. From a fundamental perspective, transition of liquid crystal into mesomorphic solid adds a new dimension to the traditional view of transition from isotropic liquid into isotropic solid. The differential scanning calorimetric thermograms compiled in Fig. 93.44 serve to distinguish a GLC from a conventional liquid crystal.

Heating a conventional liquid crystal causes a first-order transition from crystalline solid to liquid crystal at its melting point T_m followed by a transition into isotropic liquid at its clearing point T_c. In contrast, a stable GLC undergoes a second-order transition from mesomorphic solid into liquid crystal at T_g, without modifying the molecular order, followed by a transition into isotropic liquid at T_c. Intermediate between a conventional liquid crystal and a stable GLC lies an unstable GLC, which tends to recrystallize from mesomorphic melt above T_g upon heating with subsequent melting to liquid crystal at T_m and clearing at T_c. Empirically, T_g/T_m was found to fall between 2/3 and 3/4 on an absolute temperature scale.

The very first attempt to synthesize GLC's in 1971 yielded materials with a low T_g and poor morphological stability.[15] In parallel to low-molar-mass GLC's, liquid crystalline polymers have been explored for the past three decades.[16–18] In essence, GLC's are advantageous in their superior chemical purity and favorable rheological properties.[19] Existing GLC's can be categorized into (a) laterally or terminally branched, one-string compounds with a T_g mostly around room temperature;[20] (b) twin molecules with an above-ambient T_g, but generally lacking morphological stability;[21–24] (c) cyclosiloxanes functionalized with mesogenic and chiral pendants;[25–27] (d) carbosilane dendrimers exhibiting a low T_g,[28–30] and (e) macrocarbocycles with mesogenic segments as part of the ring structure.[31]

Representative structures are presented in Fig. 93.45, where $G\,x$°C Nm or $Ch\,y$°C I expresses a T_g and a T_c (for a nematic or cholesteric to isotropic transition) at x and y°C, respectively. Based on the previously reported structures, there does not seem to be a systematic approach to the design of glassy liquid crystals. Specifically, the structural factors determining the type of mesomorphism, T_g and T_c, and the stability against recrystallization from the glassy state have remained largely elusive. Glassy cholesteric liquid crystals capable of selective wavelength reflection are of particular interest because of the relevance to tunable reflective coloration.

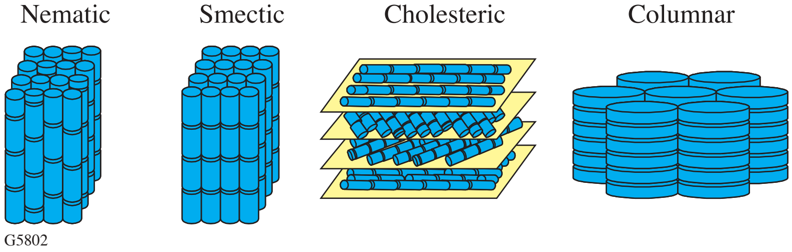


Figure 93.43
Liquid crystalline order via molecular self-organization.

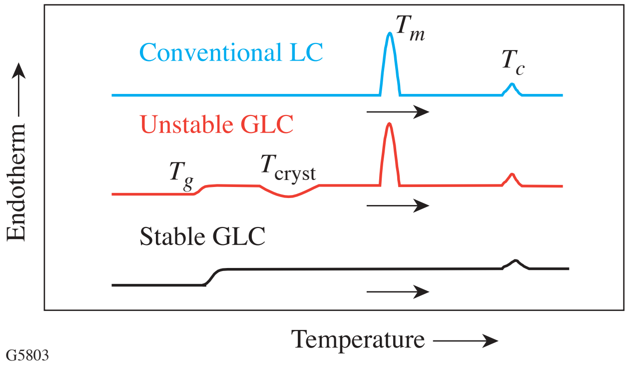


Figure 93.44
DSC thermograms of liquid crystals.

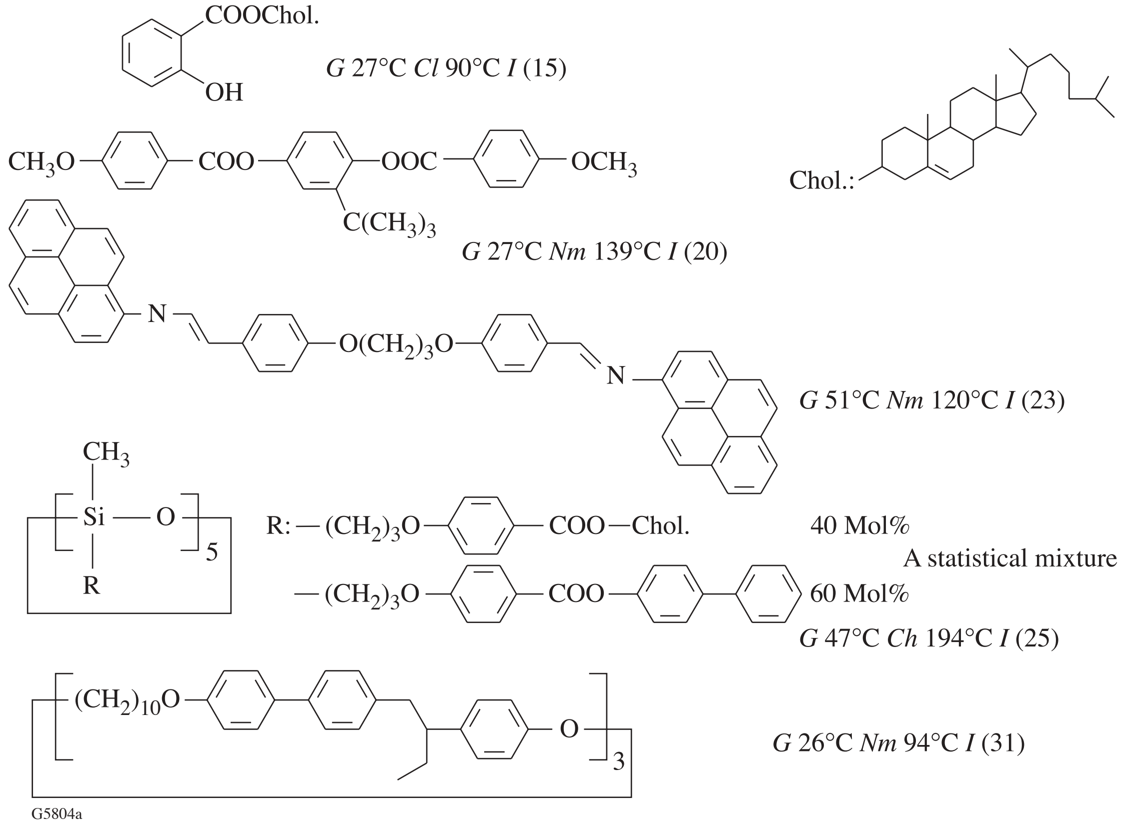


Figure 93.45
Representative glassy liquid crystals reported previously.

Optical Properties of Cholesteric Liquid Crystal Films

A cholesteric liquid crystal contains both nematic and chiral moieties in a single molecular entity or as a binary mixture. Consisting of a helical stack of quasinematic layers, a well-aligned cholesteric film can be characterized by handedness and helical pitch length p, as depicted in Fig. 93.46.

Handedness describes the direction in which twisting of the nematic director occurs from one layer to the next, and p is defined as the distance over which the director rotates by 360°. The property of selective reflection can be described in terms of $\lambda_R = p\left(n_e + n_o\right)/2$, in which n_e and n_o are the extraordinary and ordinary refractive indices of the quasi-nematic

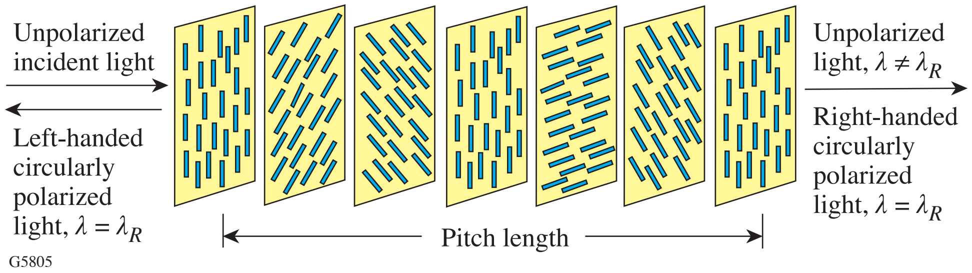


Figure 93.46
Selective reflection by a left-handed cholesteric film.[32]

layer, respectively. The other parameter of interest is the helical twisting power, a measure of the ability of a chiral moiety to generate a given helical pitch length. Let us consider incident unpolarized white light propagating through a left-handed film as illustrated in Fig. 93.46. Natural (i.e., unpolarized) light consists of equal amounts of left- and right-handed (LH and RH) circularly polarized components. The LH circularly polarized component in the neighborhood of λ_R is selectively reflected, while the RH component is completely transmitted. The selective reflection bandwidth is determined by optical birefringence, $\Delta n = n_e - n_o$. A sufficiently thick, single-handed cholesteric film is capable of reflecting 50% of incident unpolarized light within the selective reflection band. Outside the selective reflection band, incident light is transmitted regardless of its polarization state. It follows that a stack of RH and LH films tuned at the same λ_R will reflect 100% of incident unpolarized light within the selective reflection band without attenuating the rest of the spectrum.

A New Approach to Glassy Liquid Crystals with Elevated Phase Transition Temperatures and Superior Morphological Stability

Most existing liquid crystals tend to crystallize when cooled to below their melting points, thus losing the desired molecular order characteristic of liquid crystals and resulting in polycrystalline films that scatter light or limit charge transport. As an emerging class of advanced materials, GLC's preserve varied forms of molecular order characteristic of liquid crystals in the solid state. To prevent spontaneous crystallization, we have implemented a molecular design strategy in which mesogenic and chiral pendants are chemically bonded to a volume-excluding core. While the core and the pendant are crystalline as separate entities, the chemical hybrid with a proper flexible spacer connecting the two readily vitrifies into a GLC when cooled. A definitive set of GLC's has been synthesized and characterized[33–43] as summarized in Fig. 93.47, where *G x*°C (*Nm*, S_A, or *Ch*) *y*°C *I* expresses a T_g and a T_c (for a nematic,

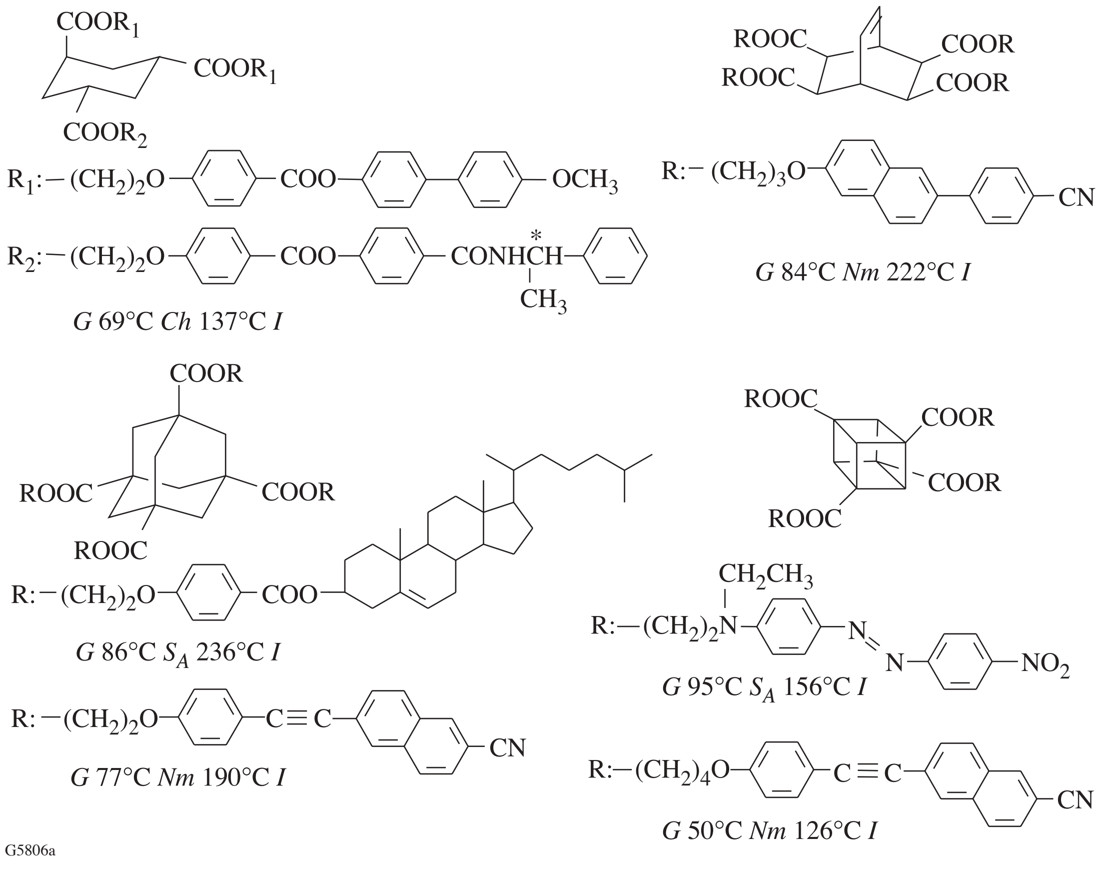


Figure 93.47
Representative morphologically stable glassy liquid crystals.

smectic A, or cholesteric to isotropic transition) at *x* and *y*°C, respectively. Cyclohexane, bicyclooctene, adamantine, and cubane serve as the cores to which nematic and chiral pendants are attached, a manifestation of the versatility of our design concept. A spacer length of two to four methylene units was found to be optimum for vitrification with an elevated T_g.

Major advances have been made recently using a cyanoterphenyl nematogen, with an exceptionally high T_m and T_c, in the construction of GLC's with substantially elevated transition temperatures without compromising morphological stability. Note the glassy nematics with a T_g close to 130°C and a T_c close to 350°C,[44] the highest values ever achieved in GLC's. As shown in Fig. 93.48, a linear nematogen is superior to an angular one in terms of phase transition temperatures. Glassy cholesterics have been synthesized in the past via a statistical approach, which requires intensive purification of a multicomponent reaction product.[45] A deterministic synthesis strategy, as described in Reaction Scheme 1, produced enantiomeric glassy cholesterics with an identical molecular structure except opposite chirality.[46]

The mixture of (I) and (II) in Reaction Scheme 1 at a mass ratio of 42 to 58 showed a T_g at 67 and a T_c at 131°C. The polarization spectra of single-handed glassy cholesteric films are shown in Fig. 93.49. An unpolarized incident beam is decomposed into two circularly polarized components of equal intensities propagating in opposite directions. Since handedness of circularly polarized light can be reversed via reflection from a specular surface, essentially 100% circular polarization of an unpolarized light source can be accomplished. An optical notch filter consisting of a stack of glassy cholesteric films of opposite handedness is shown in Fig. 93.49 to yield an attenuation of 3.75 optical density units, equivalent to a contrast ratio of better than 5000 to 1, representing the best performance of organic materials to date. The spectral range intended for

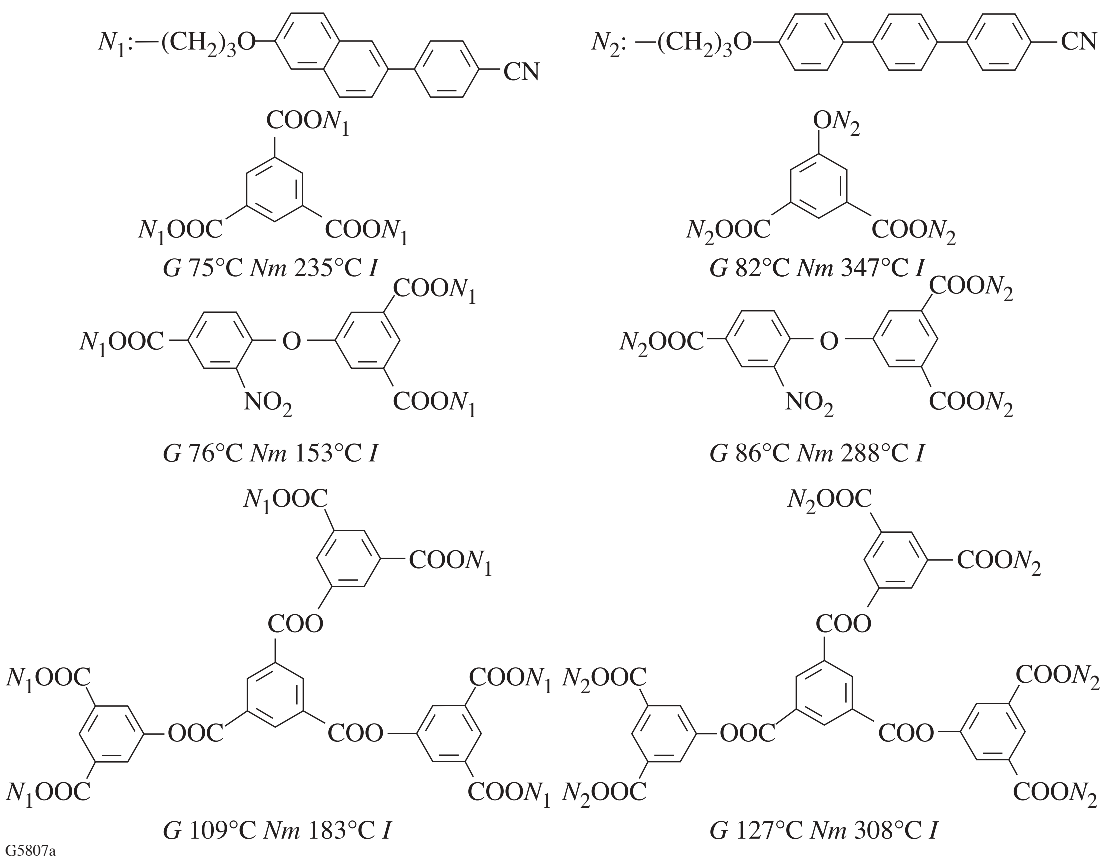
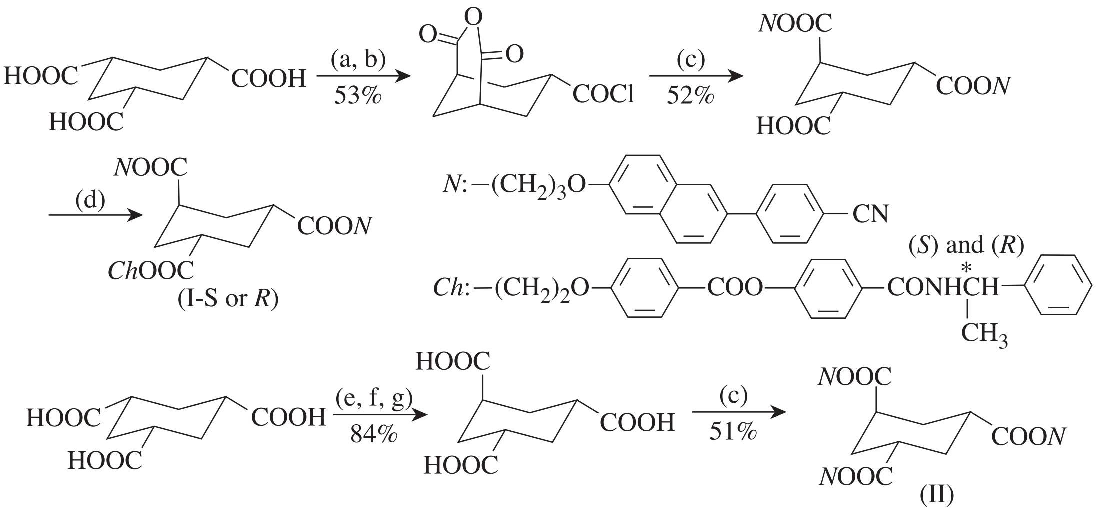


Figure 93.48
High-temperature glassy nematics.



Reaction Scheme 1
Deterministic synthesis of glassy cholesterics.

(a) $(CH_3CO)_2O$/reflux; (b) $SOCl_2$/reflux; (c) *N*OH/DMAP/Et_3N; (d) *Ch*OH/DEADC/PPh_3;
(e) $(CH_3CO)_2O$, CH_3CO_2Na; (f) CH_3COCl; (g) H_2O
DMAP: 4-(dimethylamino)pyridine; DEADC: diethyl azodicarboxylate; PPh_3: triphenylphosphune

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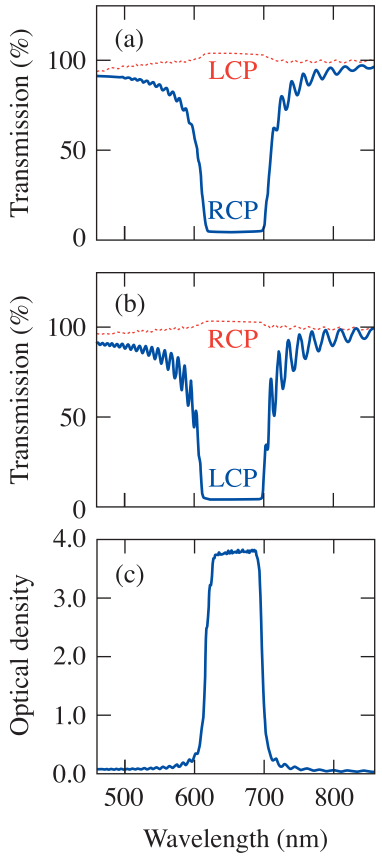

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Figure 93.49
Optical spectra of an unpolarized beam through (a) a right-handed, (b) a left-handed glassy cholesteric film, and (c) a notch filter comprising the two single-handed films (reproduced with permission from Ref. 46; copyright 2000 Wiley-VCH).

polarization and reflection can be readily tuned by varying the chemical composition.

The cyanoterphenyl group has also been successfully implemented in high-temperature glassy cholesterics synthesized in a deterministic fashion using the 5-oxyisophthalate linking unit, as shown in Fig. 93.50. Note that *G x*°C *Ch y*°C *I* expresses a T_g and a T_c (for cholesteric to isotropic transition) at *x* and *y*°C, respectively, determined from a differential scanning calorimetry (DSC) heating scan. The DSC cooling scan is presented as *I w*°C *Ch z*°C *G*, indicating a T_c (for isotropic to cholesteric transition) and a T_g at *w* and *z*°C, respectively.

Tunable Reflective Coloration by Glassy Cholesteric Films

Two distinct modes of coloration exist in nature: *pigmentary*, involving electronic transitions of chromophores underlying light absorption and emission; and *structural*, involving interference, diffraction, or scattering of ambient light by nanostructures.[47] Examples of structural colors include butterfly wings, bird feathers, and beetle cuticles. In particular, beetles' exocuticles resemble cholesteric liquid crystalline films capable of selective wavelength reflection with simultaneous circular polarization, giving rise to long-lasting brilliant colors. A wide variety of cholesteric liquid crystalline materials have been developed, such as low-viscosity liquids, lyotropic and thermotropic polymers, liquid crystal/polymer composites, and glassy liquid crystals. Of particular interest are glassy liquid crystals that resist spontaneous crystallization through heating-cooling cycles, such as mixtures of Compounds (III) and (IV) depicted in Fig. 93.51. Although (IV) crystallizes upon heating to 95°C, both (III) and its binary mixtures with (IV) form stable glassy cholesteric films.[45] Also shown in Fig. 93.51 are the selective reflection bands ranging from blue to green, red, and the infrared region with mixtures at an increasing ratio of (IV) to (III).

Furthermore, the selective reflection band and its width were shown to be tunable, albeit irreversibly, via photoracemization of a bridged binaphthyl dopant.[48] In particular, phototunability is demonstrated in Fig. 93.52, where UV irradiation of a cholesteric film at a temperature above its T_g (i.e., 120°C versus 68°C) over an increasing time period followed by cooling to room temperature is shown to result in an increasing selective reflection wavelength. Morphologically stable GLC's that resist crystallization upon heating and cooling are the key to the successful implementation of this device concept.

Reversible Tunability of Reflective Coloration

Reversible tunability of reflective coloration has been extensively explored with temperature, pressure, electric field, and light as the external stimuli.[49–57] The approach based on photoisomerization appears to be the most promising. The concept was first demonstrated by Sackman,[54] and revisited recently by Ikeda *et al.*,[55] based on *cis*-to-*trans* isomerization of azobenzene dopants in cholesteric fluid films. Shibaev *et al.*[56] employed a chiral azobenzene, both as a dopant and as a comonomer, in a polymer system with an ambient T_g and a response time of tens of minutes. Tamaoki *et al.*[57] used a glassy cholesteric matrix containing an azobenzene dopant, a material system allowing for photomodulation of pitch length at temperatures above T_g followed by cooling to below T_g to preserve the modified pitch in the solid state. All these approaches employing azobenzenes to tune reflective coloration suffer from fatigue and thermally activated *cis*-to-*trans* isomerization. Photoinduced interconversion between nematic and

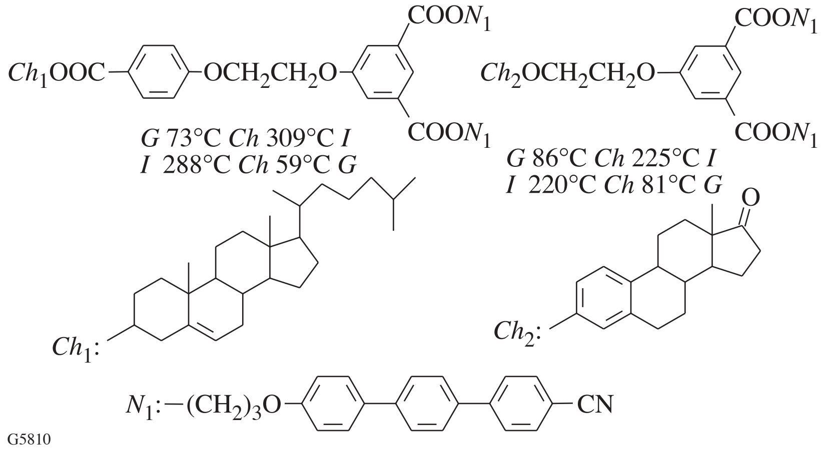

Figure 93.50
High-temperature glassy cholesterics.

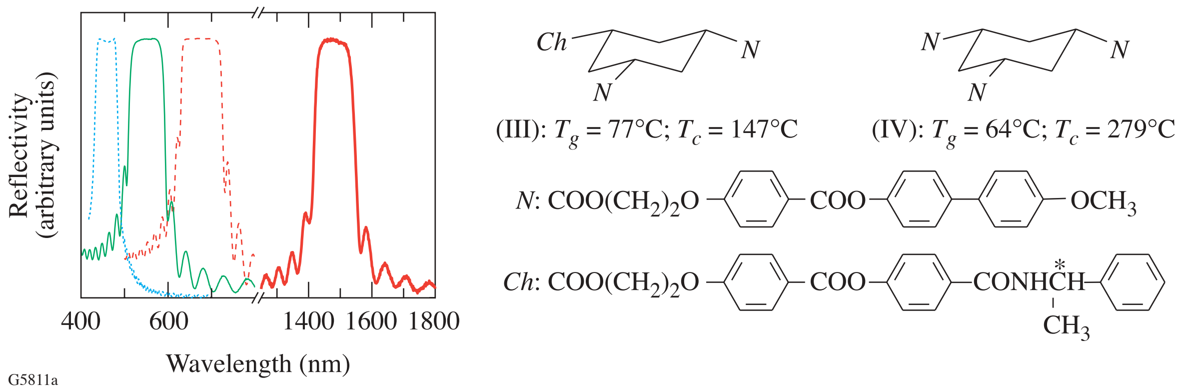

Figure 93.51
Reflective coloration by glassy cholesteric films.

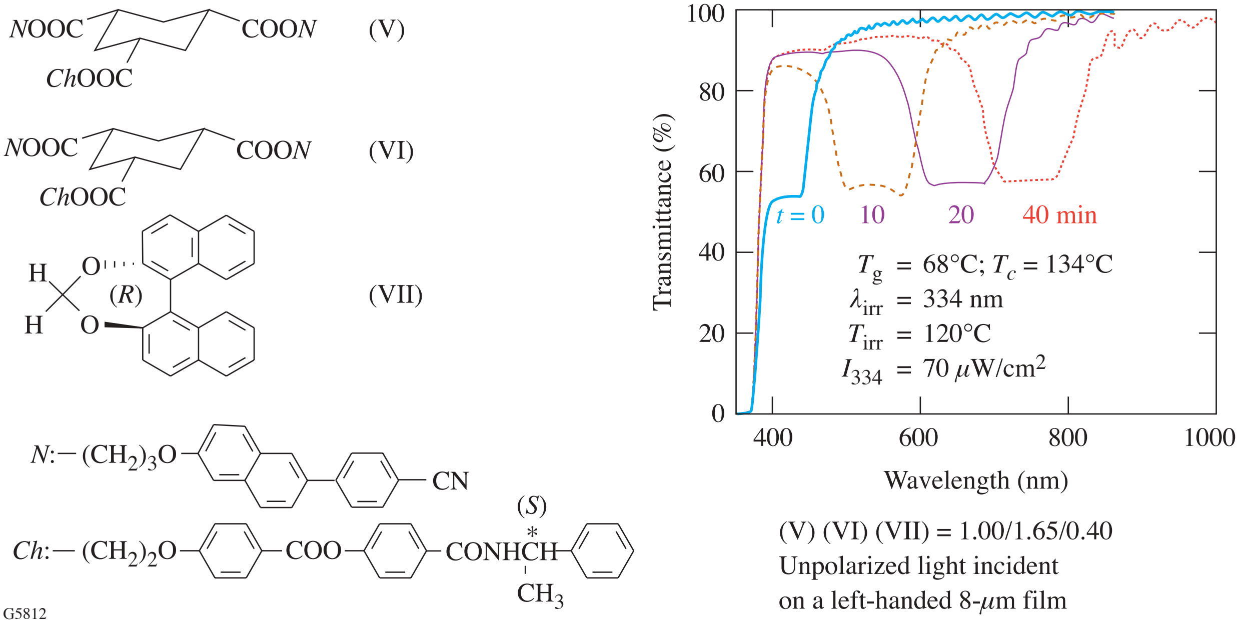

Figure 93.52
A phototunable glassy cholesteric film.

cholesteric mesomorphism and that between the right- and left-handed cholesteric mesomorphism have also been reported,[58–63] where a helical pitch length of the order of 10 μm was observed.

Of all the photoresponsive moieties that have been explored, diarylethenes[64] appear to be the most promising in terms of thermal stability and fatigue resistance. The premise is that the two interconvertible isomers, viz., the open and closed forms, present disparate helical twisting powers in a liquid crystal matrix. Indeed, the closed form of chiral diarylethenes was found to have a stronger helical twisting power than the open form in nematic liquid crystal hosts with a helical pitch length of the order of 10 μm in all cases.[62,63] To accomplish tunable reflective coloration in the visible region, a cholesteric liquid crystal with a short pitch length must be used as the host to define the base case. Moreover, glassy liquid crystal films are much preferred over liquid crystal films in practical application. Isomerization of diarylethenes was found to take place not only in liquid but also in single-crystalline[64] and amorphous[65,66] solids without altering the morphology. Modulation of pitch length, however, requires a relative rotation between quasi-nematic layers as depicted in Fig. 93.46, a macroscopic rearrangement allowable only in the liquid state; therefore, we aim at cholesteric GLC's containing diarylethene moieties.

A Novel Class of Photoresponsive GLC's

Reversible tunability of reflective coloration using diarylethene-containing GLC's is envisioned in Fig. 93.53. A glassy cholesteric film comprising the open form of a diarylethene moiety with a predetermined reflection wavelength λ_R^0 is heated to above its T_g, where irradiation at λ_1 is performed to afford the closed form. This treatment results in a shorter reflection wavelength λ_R^c, which can be preserved in the solid state with subsequent cooling to below T_g. The more-extended conjugation of the closed form could cause light absorption in the visible region. With λ_R^c frozen in the solid state, irradiation of the closed form at λ_2 will regenerate the open form, thereby bleaching the undesired absorptive color without altering λ_R^c, a clear advantage over the use of liquid films. As dictated by the open form, subsequent heating to above T_g will recover λ_R^0, which can then be frozen in the solid state by cooling through T_g. To attain the envisioned phototunability, we have developed the first diarylethene-containing nematic and chiral glasses. The molecular structures are depicted in Fig. 93.54, where *N* and *Ch* denote a nematic and a chiral moiety, respectively. Work is in progress to take advantage of these novel glassy materials together with the high-temperature GLC's shown in Figs. 93.48 and 93.50 for reversible tunability of reflective coloration with superior thermal stability and fatigue resistance.

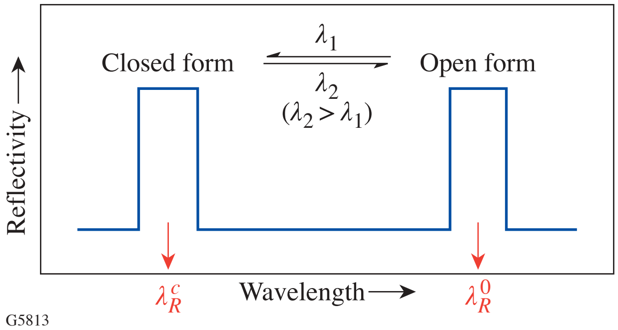

Figure 93.53
Reversible phototunability of reflective coloration.

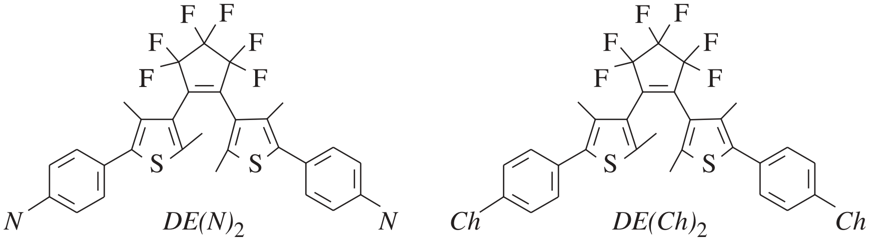

Figure 93.54
Novel glassy materials containing photoresponsive diarylethenes.

Conclusions

Glassy liquid crystals with elevated glass transition and clearing temperatures, a broad mesomorphic fluid temperature range, and excellent morphological stability have been developed for a diversity of photonic applications. In particular, glassy cholesteric films have been demonstrated for high-performance circular polarizers, optical notch filters, and reflectors across a spectral range that can be tuned by varying the chemical composition or by UV irradiation, albeit irreversibly. The molecular design concept governing glassy liquid crystals has been generalized to photoresponsive material systems containing diarylethenes, thereby enabling reversible tunability of reflective coloration with superior thermal stability and fatigue resistance.

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