Novel Photochromic Cholesteric Liquid Crystal Siloxane

Recently there has been considerable interest in the synthesis of photosensitive liquid crystalline polymers for possible applications in optical imaging systems.[1-6] Reversible phase transitions in these liquid crystalline polymers induced by photochemical isomerization of side-chain chromophores such as azobenzene and its derivatives have been observed.[2-6] Cholesteric liquid crystal siloxanes containing azobenzene moieties have potential applications in reversible holographic optical data storage media.[6] The combination of photochromic and liquid crystalline properties in the same molecule renders the material useful for many practical applications including imaging technology, optical storage materials, integrated optical devices, laser optical media, and nonlinear optical (NLO) materials. Synthesis of materials exhibiting both photochromic and liquid crystalline properties is challenging as their combination usually results in the loss of one of these properties.

Recently, there have been reports of nematic liquid crystal polymers in which the side chains were partially composed of spiropyran or spiroxazine units.[7-11] Irradiation of these copolymer liquid crystalline films with UV radiation turned the films blue due to the formation of the merocyanine structure. This process was reversible with the application of heat and light (>500 nm).[7-11] The noncentrosymmetric geometry of the merocyanine structure leads to possible second-order (χ^2) nonlinear optical applications. Previous work has shown that the merocyanine form of spiropyran in liquid crystal polymers can be aligned by poling in an electric field with a resulting second-order nonlinear response.[11] In our continuing efforts to develop new liquid crystal polymers with covalently attached NLO chromophores, we have synthesized a cholesteric cyclic siloxane liquid crystalline molecule containing spiropyran units. To our knowledge, this is the first report of a cholesteric photochromic liquid crystalline siloxane containing a spiropyran molecule. The liquid crystal not only exhibits the unique optical properties of cholesteric liquid crystals (selective reflection and large optical rotatory power) but it also exhibits photochromism in thin films, in fibers, and in solution.

The liquid crystalline siloxane, Figure 1a, was prepared by a hydrosilylation reaction between cyclic (pentamethylhydro)siloxane (Petrarch) and a combination of cholesteryl 4-(allyloxy)benzoate (CAB), biphenyl 4-(allyloxy)benzoate (BAB), and (allyloxy)benzoate nitrobenzospiropyran (ABNS) mesogens. The relative molar ratios of these terminal vinyl-containing mesogens attached to each five-membered ring was 0.45:0.45:0.1 for CAB/BAB/ABNS. The mixture of alkenes (0.14 g of BAB, 0.23 of CAB, and 0.04 g of ABNS, 10 mol % excess versus Si–H groups) was dissolved in dry toluene (35 mL), and the solution was heated to 60 °C under dry argon. The pentamethylsiloxane was added (50 μL) by syringe, and 100 μL of dicyclopentadienylplatinum(II) chloride catalyst (in methylene chloride) was added to give a Pt/alkene mole ratio of approximately 1:10^3. Reaction progress (completion in 4 h) was followed with FTIR (Perkin-Elmer 1725X) by monitoring the disappearance of the Si–H band at 2150 cm^{-1} on thin films cast on silver chloride plates. Purification of the product by repeated precipitation from toluene using methanol was followed by thin-layer chromatography (TLC) (silica plates, methylene chloride as eluent) to ensure no excess alkene remained in the product. TLC[12] has been shown to be a sensitive analytical technique in the measurement of residual alkenes in liquid crystalline polysiloxanes.

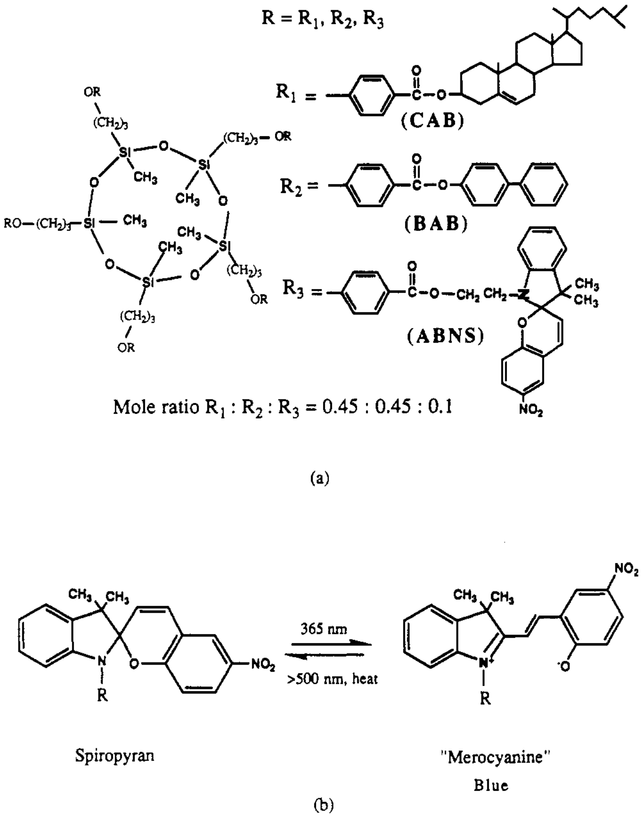

Figure 1. Liquid crystalline siloxane with three different mesogens attached (a) and characteristic photochromic reaction of spiropyran (b). The mesogens, CAB, BAB, and ABNS, are shown excluding their allyloxy units.

The (allyloxy)benzoic acid leader group was synthesized according to published procedures.[13] Cholesterol (Aldrich), hydroxybiphenyl (Aldrich), and (hydroxyethyl)nitrobenzospiropyran (1′-β-(hydroxyethyl)-6-nitro-3′,3′-dimethylspiro(2*H*-1-benzopyran-2,2′-indoline)) (Chroma Chemicals, Dayton, OH) were attached to this leader group using an esterification reaction described by Hassner and Alexian[14] using (dimethylamino)pyridine (Aldrich) as the catalyst. The products were purified by repeated recrystallization from appropriate solvents and column chromatography. The structures of the pendant mesogens were confirmed by elemental analysis and FTIR.

The resulting hydrosilylation product exhibited two thermal transitions as observed with differential scanning calorimetry (DSC) (Du Pont 910 DSC). A glass transition of 51 °C followed by a clearing temperature of 210 °C were obtained from second heating runs with a heating rate of 10 °C/min. Polarized optical microscopy (POM) confirmed the liquid crystalline phase present between these temperatures was cholesteric. Upon cooling from the isotropic phase, a tight focal-conic texture characteristic of cholesteric materials was observed.[15] Displacement of the top cover glass slip resulted in the reorientation of the random helices perpendicular to the glass substrates, causing a macroscopically aligned planar texture which selectively reflects circularly polarized light.[16]

The glassy nature of this siloxane allows for the cholesteric structure to be frozen into thin films. Shearing the liquid crystal between glass plates at 150 °C and subsequent cooling to room temperature yields a glassy film exhibiting a selective reflection band centered at 514 nm (Figure 2a). Reflection spectra were obtained from a

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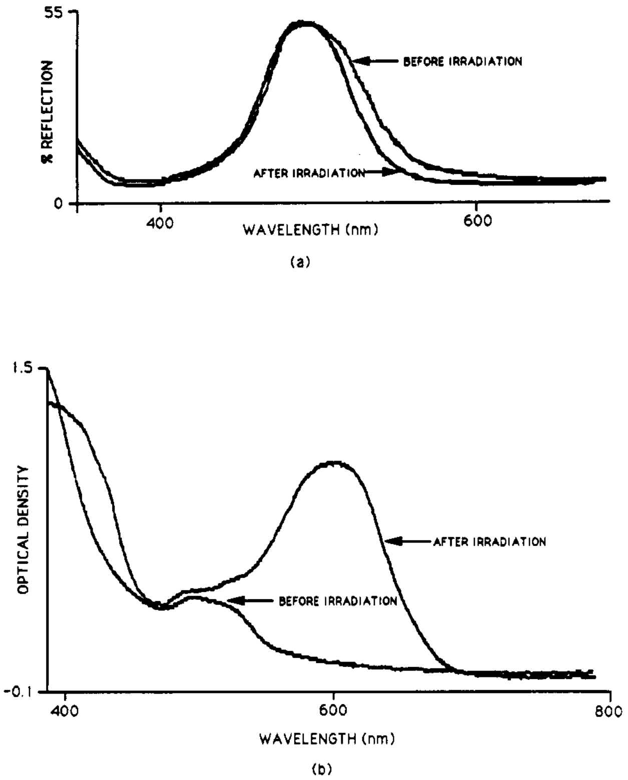

Figure 2. Reflection spectra (a) and absorption spectra (b) from glassy cholesteric liquid crystalline siloxane films before and after irradiation with UV (365-nm) light.

Perkin-Elmer Lambda 4B equipped with an integrating sphere attachment. The corresponding absorption spectra (Figure 2b) also reveal this selective reflection bandwidth as well as the characteristic UV absorption maxima of spiropyran.

Upon irradiation of the thin film with UV light (365 nm), the glassy liquid crystalline film turns blue in less than 10 s due to the characteristic ring-opening reaction (Figure 1b) of the spiropyran molecule which is now transformed to the merocyanine structure. This absorption peak, centered at 594 nm, is clearly evident in the absorption spectrum but is absent from the reflection spectra. No changes in the reflection wavelength or bandwidth were observed upon irradiation. The blue disappears slowly in the dark over a period of 20 h. The color-fading reaction involves the ring closure of the zwitterionic merocyanine form (Figure 1b). The energy barrier for the dark back reaction is known to be influenced by substituents in the spiropyran ring, polarity of the solvents, and environmental conditions. In highly viscous solvents and polymer matrices, the ring closure in the dark has been shown to proceed slowly.[17] Heating of the thin film to 45–50 °C eliminates the blue in a matter of seconds. The blue formation and disappearance are reversible, thus demonstrating the photochromic nature of this liquid crystalline siloxane. The thin films were also resistant to photofatigue.

Upon heating to the isotropic phase, the thin film of liquid remains clear (absence of red), indicating no aggregation of the spiropyran molecules, unlike the nematic copolymers synthesized by Krongauz.[7-11] Krongauz observed that, upon heating into the isotropic phase, the isotropic melts exhibited a red color, indicating the formation of aggregated merocyanine structures which lead to the physical cross-linking of the polymeric backbones. The absence of this behavior for the siloxane liquid crystal may be attributed to steric factors. Once covalently attached to the siloxane core, the mobility of these spiropyran molecules becomes restricted since each ring has five large pendant groups attached. Examinations of spiropyran-doped siloxanes containing only CAB and BAB pendant groups indicate aggregation was possible. The liquid crystal siloxane is also photochromic in solvents such as toluene and dichloromethane, exhibiting the same absorption spectra as in thin films upon irradiation. The thermal fading of the blue in toluene solutions occurs in approximately 120 s and follows first-order kinetics characteristic of spiropyrans.[17]

X-ray diffraction studies (Rigaku RU-300 rotating-anode generator, graphite monochromated Cu Kα radiation, evacuated Statton camera, sample-to-film distance to 72.9 or 170.0 mm) on thin glassy films agree well with similar cholesteric cyclic siloxane liquid crystals without spiropyran units attached.[18] This was unexpected as the attachment of the spiropyran units was lateral in contrast to the other mesogens as shown in Figure 1a. Possible steric disruptions to the liquid crystalline packing may be regulated by the flexibility of the allyloxy leader group and/or the small percentage of these lateral attachments. No differences in the small- or wide-angle scattering patterns were observed for films before and after irradiation with UV (365-nm) light. Although the film clearly turns blue indicating an opening of the spiropyran molecule, this does not disrupt the frozen liquid crystalline order.

Surprisingly, this low molecular weight siloxane can be drawn into fibers tens of meters long from the liquid crystalline mesophase. At room temperature, these fibers are glassy but maintain their liquid crystalline order. As discussed by Bunning et al.,[18] the orientation of the lamellae within these fibers is the opposite of the transverse orientation in conventional polymeric liquid crystalline fibers.[19] Fibers from this liquid crystal are easily drawn from the melt, highly birefringent, and photochromic. When irradiated with UV (365-nm) light, the fibers exhibit an intense blue which disappears slowly (20 h) in the dark. These irradiated fibers are also birefringent. Preliminary experiments performed on fibers drawn from the siloxane liquid crystal containing only CAB and BAB (50 mol % each) indicate they propagate radiation from a He–Ne laser (633-nm) light. Based on these observations, experiments are now in progress to quantitatively evaluate the transmittance of the spiropyran-containing siloxane before and after irradiation with UV light. Upon irradiation, it is expected that the blue fiber will attenuate the propagation of He–Ne radiation and thus act as a fiber-optic filter. The ease with which these liquid crystalline siloxanes are shear aligned, the order frozen at room temperature, and the high optical quality of the glasses formed make them good matrices for incorporating NLO chromophores. Liquid crystal siloxanes containing various compositions of the spiropyran mesogens are currently being investigated for second-order nonlinear responses.

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