

Novel Vitrifiable Liquid Crystals as Optical Materials**

By Shaw H. Chen,* Hongqin Shi, Brooke M. Conger,
John C. Mastrangelo, and Tersuo Tsutsui

Due to the spontaneous molecular self-assembly into various mesophases and the associated optical anisotropy, liquid crystals (LCs) have found numerous electro-optical and optoelectronic applications. There are several generic device concepts. In the now almost mature LC display technology, these materials function in the fluid state where an applied field induces molecular reorientation with a response time on the order of a millisecond. With appropriate structural moieties, LCs may also function in the solid-state via a photonic or electronic stimulus with a response time in the pico- to femtosecond range. In addition to these active devices, LCs in thin solid films can be employed as passive devices for which no switching is involved. In applications involving solid films, LCs that can be vitrified with an elevated glass transition temperature, T_g , offer long-term mesomorphic stability as well as environmental durability. Thus, both polymeric and low molar mass LCs capable of vitrification have been explored. Whereas vitrification appears to be a privilege of polymeric materials, their generally high melt viscosity and broad distribution of relaxation times have been identified as potential problems where processing into large-area thin films is desired. Therefore, we have focused on vitrifiable LCs (VLCs) in view of the ease with which they can be processed into thin films.

In a typical device fabrication process, an LC film is cooled to below its T_g upon thermal annealing in the meso-

morphic temperature range to maximize order. In principle, all liquids should vitrify at a sufficiently rapid cooling rate, but thermally-induced phase transformation may occur because of the metastable vitreous state. Nevertheless, to date both vitrification of LCs and morphological stability of resultant glasses have remained poorly understood from the perspective of molecular structure. Furthermore, the design of VLCs with an elevated glass transition temperature is particularly challenging in that a subtle structural balance must be struck between order (i.e. liquid crystalline mesomorphism) and disorder (i.e. glass). This communication reports on the molecular design of vitrifiable organic materials and their morphological stability as characterized by recrystallization from both mesomorphic and isotropic states as a function of temperature. Potential applications will be illustrated with the use of VLC films for the control of light polarization and for polarized emission.

As a rule, most low molar mass LCs will crystallize on cooling from the melt. A number of VLCs, as an exception, have also been reported; however, many of the quenched glasses tend to recrystallize on heating, an indication of morphological instability. Moreover, no common theme can be identified from all the structures that have been synthesized.^[1-11] In a recent series of papers,^[12-14] we have successfully implemented a generic design approach in which rigid, elongated mesogenic groups are attached to bulky, non-planar central cores to have the two structural elements present a volume-excluding effect on each other, as a way to avoid crystallization. Representative VLC structures with well-defined stereochemistry are depicted in Figure 1 as compounds **I** to **VII** with the exception of **III**, a chiral dopant found to recrystallize at room temperature. Note the possibility of achieving nematic, smectic, and cholesteric mesophases while possessing glass-forming ability. The versatility of this approach is further demonstrated by the ability of various alicyclics, e.g. cyclohexane, bicyclooctene, cubane, and adamantane, to serve as the central cores. In a nutshell, glass-forming ability is attributed to the partial coupling furnished by the flexible spacer connecting the pendant mesogenic group and the central core.

To investigate the morphological stability of VLCs against thermally activated recrystallization, compounds **VIII** to **XI**, as depicted in Figure 2, were synthesized and characterized.^[12] Note that these four model VLCs differ from each other mainly in the manner in which pendant cyanotolan groups are configured on the cyclohexane ring, i.e. axial as opposed to equatorial. As predicted by the secondary nucleation theory,^[15] the rate of spherulitic growth, or crystallization velocity (CV), as it is often referred to, traverses a maximum as the temperature is raised from T_g to T_m , the crystalline melting point. Thus, the experimentally determined CV data were fitted to the theory as shown in Figure 2 in the plot of temperature vs. log CV.

The question that arises is the appropriateness of using the maximum CV as a measure of morphological stability. In the context of the secondary nucleation theory, CV is de-

[*] Prof. S. H. Chen, Dr. H. Shi, B. M. Conger,
Dr. J. C. Mastrangelo
Materials Science Program
Chemical Engineering Department and
Laboratory for Laser Energetics
Center for Optoelectronics and Imaging
University of Rochester
240 East River Road
Rochester, NY 14623-1212 (USA)

Dr. T. Tsutsui
Department of Materials Science and Technology
Graduate School of Engineering Sciences
Kyushu University
Kasuga-Shi, Fukuoka 816 (Japan)

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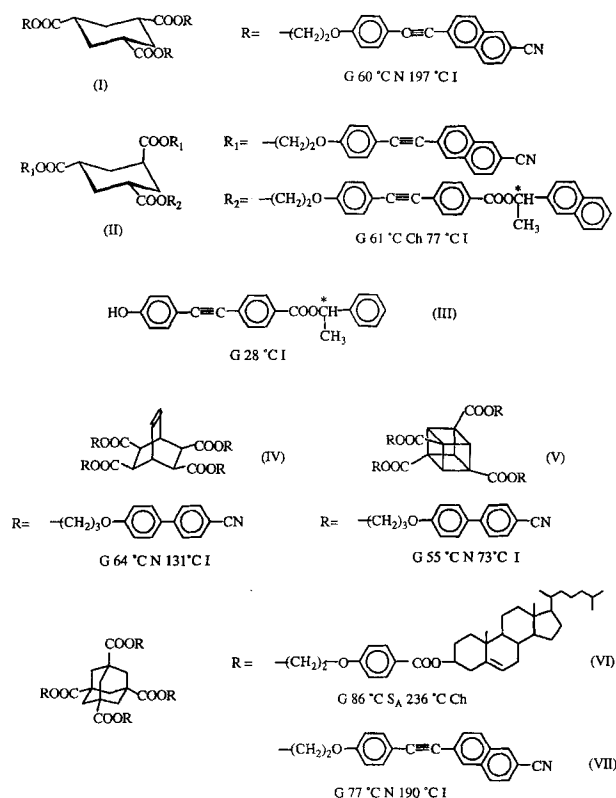


Fig. 1. Chemical structures and thermotropic properties of model VLCs **I** to **VII**, except **III**, a chiral dopant. Results obtained by DSC measurements of quenched glasses at a heating rate of 20 K/min.

terminated by the degree of supercooling, i.e. $(T_m - T)/T_m$, and by rate of molecular diffusion, as determined by T/T_g , where all temperatures are expressed on an absolute scale. Thus, the temperature at which the maximum CV occurs, denoted as T_{mcv} , is reduced with respect to T_g and T_m to account for the dependence of CV on temperature as one compound is compared with another. The fact that $T_{mcv}/T_g = 1.20 \pm 0.04$ and that $T_{mcv}/T_m = 0.92 \pm 0.01$ for all four nematic VLCs clearly legitimizes the adoption of the maximum CV as a measure of morphological stability. Based on the results plotted in Figure 2, it is concluded that the all-axial configuration yields the least stable VLC system, axial-equatorial mixed modes the most stable, whereas all-equatorial falls in between the two.

Furthermore, compound **IX**, the most stable of all, has a maximum CV of 6 nm/s, which is comparable to that of isotactic polystyrene with an $M_v = 2.1 \times 10^6$, $T_{mcv}/T_g = 1.25$, $T_{mcv}/T_m = 0.88$, and maximum CV = 4 nm/s.^[15] Hence, VLCs can be made as stable as a typical "slowly crystallizing" polymer, as isotactic polystyrene was quoted, with optimized stereochemistry. In contrast, no recrystallization was observed during thermal annealing of chiral-nematic VLCs over a period of months, presumably because of the structural dissimilarity between pendant groups, which further enhances morphological stability compared with nematic VLCs.

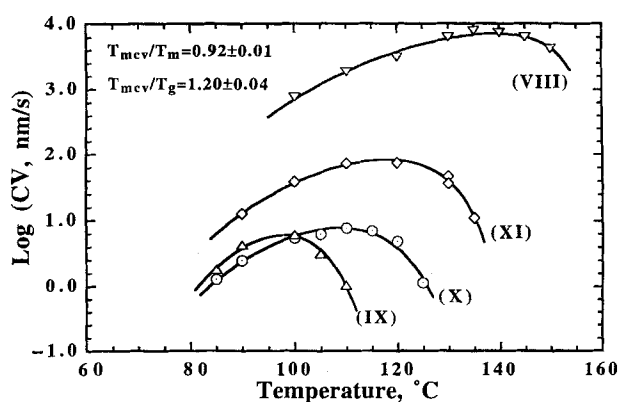
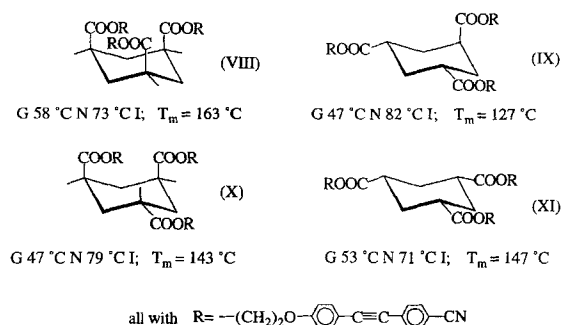


Fig. 2. Spherulitic growth measured by crystallization velocity of nematic VLCs **VIII** through **XI** as a function of temperature; the curves represent the best fit to the secondary nucleation theory.

To demonstrate the practical applications of VLCs, chiral-nematic films were prepared using blends of **II/I** and **III/I** with the same chiral mole fraction value of 0.16. The property of selective wavelength reflection is shown in Figure 3, in which the broad bandwidth is a consequence of the high optical birefringence of nematogens. Note that the side-band oscillation is an indication of the uniformity of film thickness, and the superior optical quality is evidenced by the observed optical density approaching the theoretical

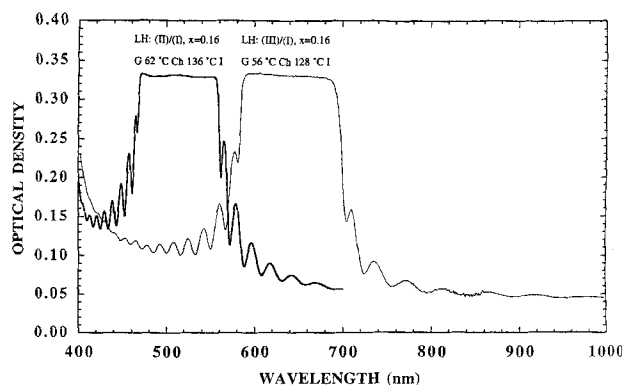
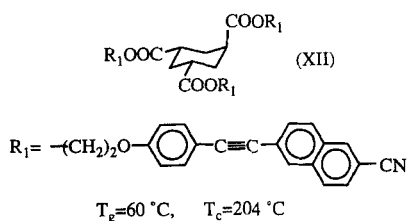


Fig. 3. UV-vis-NIR spectra results to demonstrate selective reflection by vitrified chiral-nematic LC films prepared with chiral-nematic blends, **II/I** and **III/I**, at the same chiral mole fraction.

limit of 0.30 in a perfectly aligned chiral-nematic film. The observed selective reflection from a chiral-nematic film is accompanied by circular polarization, which serves as a basis for polarized light source and color projection.^[16]

In addition, nematic VLCs are useful for the fabrication of half- and quarter-wave plates. In all of these applications, VLCs offer a unique advantage in their capability for large aperture devices, besides mesomorphic stability and environmental durability. A more challenging task is to accomplish polarized photo- and electroluminescence (PL and EL) from within the VLC films. Our first attempts^[17] in which the PL from nematic and chiral-nematic VLC films was characterized are shown in Figures 4 and 5 using compounds **XII** and **XIII**, respectively. In the case of linearly polarized PL from compound **XII**, centered on 465 nm, the polarization factor P , defined as $I_{||}/I_{\perp}$, was evaluated at 2.80 with an order parameter of 0.71 for a 5 μm thick film.

An 18 μm thick film of compound **XIII** shows a good quality selective reflection band centered at 1140 nm (see Fig. 5a), determined to arise from a left-handed helical structure, and a PL peak at 425 nm (see Fig. 5b). The dis-



Thickness (μm)	S	P
5	0.71 ± 0.02	2.88 ± 0.07
1.5	0.69 ± 0.04	2.65 ± 0.04

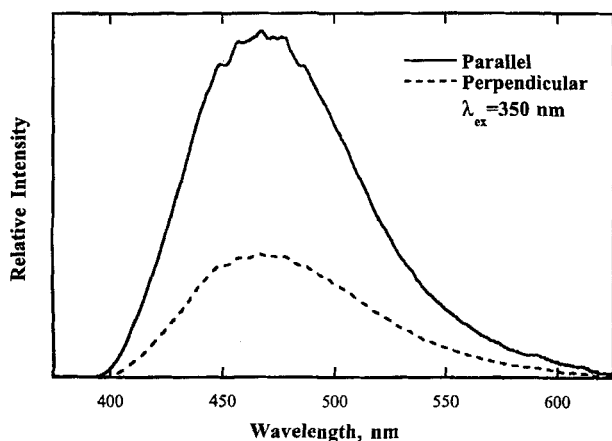
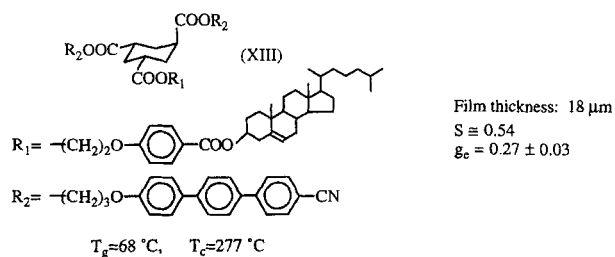


Fig. 4. Linearly polarized PL from a vitrified nematic LC film prepared with compound **XII**.



Film thickness: 18 μm

$S \approx 0.54$

$g_c = 0.27 \pm 0.03$

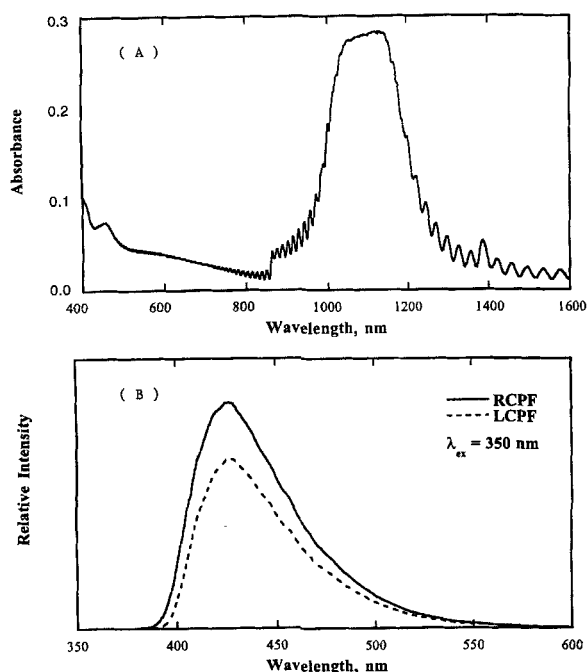


Fig. 5. a) Selective wavelength reflection of a chiral-nematic LC thin film prepared with compound **XIII**; b) circularly polarized PL from the same film.

symmetry factor, defined as $2(I_R - I_L)/(I_R + I_L)$, was found to be 0.27, with an order parameter of 0.54. These polarized PL results are quite encouraging, and we are in the process of integrating VLCs into EL devices. In view of the need for a multilayer structure to optimize EL device performance, the potential that VLCs hold for vacuum deposition represents another advantage over polymer analogues, which normally require wet processing.

In summary, a generic approach is demonstrated for the design of VLCs with an elevated value of T_g . With optimized stereochemistry, nematic VLCs can be as morphologically stable as a typical slowly crystallizing polymer. Because of the structural dissimilarity between pendant groups, chiral-nematic VLCs possess morphological stability superior to their nematic counterparts. The advantages offered by VLCs in optical applications include long-term mesomorphic stability, environmental durability, ease of processing into thin films, and the capability for large aperture. Potential applications to the control of light polariza-

tion and polarized PL have been illustrated with selected VLC samples.

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Oligo(siloxane) Rings and Cages Possessing Nickel-Containing Liquid Crystal Side Chains**

By Isabel M. Saez and Peter Styring*

The incorporation of metals into materials with designed, controllable supramolecular architectures is a challenge identified in many different areas of research.^[1] Structurally well-defined silasesquioxanes (sphaerosilicates) and cyclic siloxanes have recently attracted much attention as building blocks in the preparation of, for example, metal-containing siliceous materials,^[2] hybrid organic-inorganic materials,^[3] models for silica supported metal catalysts,^[4] discrete molecular models for the secondary building unit of zeolite A,^[5] metal-modified electrode surfaces,^[6] the

backbone of cross-linked, highly porous materials,^[7] and as the framework of multi-metallic compounds.^[8] The wealth of molecular structures derived from these highly versatile inorganic building blocks has led us to incorporate them into the skeleton of side-chain, metal-containing liquid crystals, free from cross-linking. This results in oligomeric materials which lie at the interface between side-chain liquid crystal polysiloxanes and silica surface supported metal complexes.

Metal-containing liquid crystalline (metallomesogenic) polymers are of considerable interest^[1b,9] since the incorporation of a metal center into a mesomorphic polymeric material could produce processable systems with interesting applications. The major synthetic drawback is that metallomesogens of divalent metals derived from bidentate ligands tend to be symmetrical. Polymerization of such bifunctional monomers leads to either a metallomesogen-containing backbone or a cross-linked side-chain liquid crystal polymer. In the latter case, only small degrees of cross-linking are tolerated before liquid crystallinity is lost. Therefore, a major challenge, identified recently by Oriol and Serrano,^[9] involves the synthesis of mono-functionalized metallomesogenic monomers.

In this paper we report the results of an investigation into the synthesis of a new non-symmetrical chelating ligand (**1**), the synthesis of the non-symmetrical, mono-functionalized diamagnetic nickel(II) complex (**2**), and the incorporation of the complex into pre-formed hydrosiloxane ring and cage structures (**3** and **4**) of known molecular weight and topology (Scheme 1). This results in metallosiloxanes which are free from cross-linking of the metallomesogenic monomers. These materials are of potential importance in a number of areas of research. Grafting anisotropic metal-containing complexes onto isotropic siloxane supports allows us to immobilize the liquid crystal at a single point on a predefined matrix, yet because of the absence of cross-linking, the mesogenic unit is effectively decoupled from the three-dimensional order of the backbone and is free to align with an applied field. This allows us to combine the processability and mechanical stability of polymeric materials with the unique electronic, optical, nonlinear optical, and magnetic properties of metal-containing liquid crystals. Having materials with well-defined degrees of polymerization, low polydispersity and a defined topology means that accurate structure-property correlations may be identified in these and related materials.

The aim was to synthesize pro-mesogenic ligands in which the two ends of the molecule are composed of different intermediates. Salicylaldehyde and 1,3-dicarbonyl subunits therefore represent an ideal entry point into such systems. The unsymmetrical ligand (**1**) was prepared by the reaction of equimolar quantities of phenylmalonaldehyde, 5-oct-9-enyloxysalicylaldehyde, and 1,2-diaminoethane in dichloromethane under reflux with the azeotropic distillation of water. The ¹H NMR spectrum of **1** exhibits four unique resonances in the region 13.5 to 7.5 ppm. These have

[*] Dr. P. Styring, Dr. I. M. Saez
School of Chemistry, The University of Hull
Hull HU6 7RX (UK)

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