

**THE LIQUID CRYSTALS BOOK SERIES**

**CROSS-LINKED  
LIQUID CRYSTALLINE  
SYSTEMS**

**FROM RIGID POLYMER NETWORKS TO ELASTOMERS**

# THE LIQUID CRYSTALS BOOK SERIES

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The Liquid Crystals book series publishes authoritative accounts of all aspects of the field, ranging from the basic fundamentals to the forefront of research; from the physics of liquid crystals to their chemical and biological properties; and from their self-assembling structures to their applications in devices. The series will provide readers new to liquid crystals with a firm grounding in the subject, while experienced scientists and liquid crystallographers will find that the series

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# CROSS-LINKED LIQUID CRYSTALLINE SYSTEMS

FROM RIGID POLYMER NETWORKS TO ELASTOMERS

Edited by  
Dirk J. Broer  
Gregory P. Crawford  
Slobodan Žumer



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# Preface

Liquid crystals are a special class of materials in nature, hence their name is a deliberate oxymoron to describe a material system that exhibits hybrid properties—physical properties manifested by both liquids and crystals. Because of their application success in flat-panel displays and application potential in many other areas, they have attracted significant interest from both the applied and basic research communities. Like liquid crystals, polymers are unusual materials in many respects. Polymers have also enjoyed a great deal of research attention because of their vast applications and uses and complex fundamental properties. We have now learned that the combination of liquid crystal and polymer properties produces a broad array of new effects that are not simply manifestations of either native liquid crystals or polymers alone. One embodiment includes densely cross-linked networks created from reactive mesogen materials: the liquid crystalline order can be manipulated by external constraints—such as surfaces, electric or magnetic fields, or shear forces—to create a temporary, and otherwise unstable, configuration that can indefinitely be captured through photopolymerization. These highly ordered and optically transparent films have found their way into the commercial market on nearly all desktop liquid crystal display screens to compensate for the viewing angle or to improve on their contrast. On the other end of the spectrum, elastomers are weakly cross-linked systems that can give rise to spontaneous shape changes of several hundred percent, and by the application of stress or stain, they can exhibit some unusual mechanical–optical effects. Liquid crystal elastomers are being considered for a number of applications, including such breakthrough possibilities as the artificial muscle.

The worldwide need for flat-panel displays drove much of the fundamental research in the field of liquid crystals, making that application of paramount interest to the liquid crystal community. That field is maturing, and much of the applied research is now looking for alternative uses of liquid crystal materials. With the greatly expanding interest in liquid crystalline polymers and elastomers, researchers are now looking into application areas for these unique materials, which range from passive optical elements on displays to far-reaching concepts such as artificial muscles, tunable lasers, actuators, membranes, and spectrometers. This new application space is broad and far reaching. There is currently no comprehensive account that brings together the fundamental materials aspects of liquid crystalline polymer and elastomer systems, their interconnections and interdisciplinary scope, and their broad application potential.

Liquid crystal displays were discovered in the 1960s, and today we are enjoying the benefits of that fundamental discovery and its translation into products. Densely cross-linked liquid crystal systems and liquid crystal elastomers were proposed in the 1980s, two decades after the liquid crystal display and a century after the discovery of the liquid crystal phase itself. In retrospect, liquid crystal display technology drove much of the fundamental research in liquid crystals. The systems' ability to enforce three-dimensional structure in the molecular order and capture it created a number



of compelling application possibilities because it provided necessary control of the molecular order. The methods to produce such structures are limited in number, and no process enabled such control until the discovery of photopolymerizable liquid crystal systems. As these systems became more available, fundamental studies ensued and many other applications followed, beyond the optical compensator, such as broadband polarizers, actuators, reorientable microstructures, and so forth.

Unlike the densely cross-linked liquid crystal polymer, the molecular structure of a liquid crystal elastomer is similar to that of a traditional rubber: it consists of long chains of molecules that can easily slip past one other and so enable the material to be expanded with very little force. Attached to the elastomer chains, like the branches of a tree, are smaller rod-like molecules that are usually found in liquid crystals. These liquid crystal moieties allow the material to interact with light and can align the long chains and give unexpected mechanical properties, such as the ability to change color when they are stretched and the ability to dramatically change their shape when they are heated, or, for certain renditions of compounds, when light impinges upon them. Liquid crystal elastomers have a variety of potential uses. For example, they could provide the basis for a laser which needs only a small amount of power to operate and can change its emission just by being stretched. The natural twisting of their internal structure means liquid crystal elastomers could act as a new system for identifying the difference between right-handed and left-handed forms of drug compounds. On the fundamental side, liquid crystal elastomers experience certain shape changes with little or no energy cost. This has been dubbed “soft elasticity” and places these materials in a unique class—those between liquid and solid in an elastic classification of matter.

As a scientist or engineer, you will find upon reflection that there seems to be no shortage of fundamental science, unusual properties, and far-reaching applications in densely crossed-linked liquid crystal systems and liquid crystal elastomers. After some 25 years of research, the science and application possibilities seem endless. These systems provide a rich new avenue for both fundamental and applied research and continue to fascinate scientists and engineers who think broadly about their complexity, physical phenomena, synthetic features, and uses. In this volume, for the first time, we bring together those systems and their variations. We have attracted some of the most creative and influential experts in the field to contribute on their innovative science and application. The field, much like traditional liquid crystals, is one of an interdisciplinary nature with a broad spectrum, from the very fundamental questions of nature to a myriad of practical uses. We hope that our efforts in compiling this text will advance the understanding of basic science behind these systems, accelerate some of the proposed applications to the marketplace, and inspire generations of scientists to think broadly about these exciting and useful materials.

We thank Mr. M. Vavptic for conversion and improvement of figures that were not prepared according to the T&F prescription and for preparation of the Index.

**Dirk J. Broer**  
**Gregory P. Crawford**  
**Slobodan Žumer**

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# Editors

**Dirk J. Broer** is a polymer chemist (PhD—University of Groningen, the Netherlands) and is specialized in polymer structuring and self-organization. He joined Philips Research in Eindhoven, the Netherlands in 1973 where he worked on a wide variety of topics. Some representative examples are vapor-phase polymerization, optical data storage, telecommunication fibers, and liquid crystal networks. Between 1990 and 1991 he worked at the DuPont Experimental Station in Delaware, United States on nonlinear optical materials and vapor-phase deposition of  $\pi$ -conjugated polymers. In 1991 he began developing optical films for LCD enhancement at Philips Research and in 2000 he started his work on new manufacturing technologies of LCDs for large area displays and electronic wallpaper. From 2003 to 2010, Dirk J. Broer was appointed as senior research fellow and vice president at the Philips Research Laboratories specializing on biomedical devices and applications of polymeric materials.

In 1996 Dirk J. Broer became a part-time professor at the Eindhoven University covering research topics as liquid crystal orientation, polymer waveguides, solar energy, organic semiconductors, nanolithography, soft lithography, and polymer actuators. In 2010 he became a fulltime professor in Eindhoven University specializing in functional organic materials for clean technologies as energy harvesting, water treatment, and healthcare applications. Special emphasis is given to responsive polymers that morph under the action of heat, light, electrical, and magnetic fields or driven by contacts with agents and/or changes in their ambient conditions and to membrane technology with monodisperse nano-porosity.

He has coauthored more than 200 publications in peer-reviewed journals and holds more than 80 U.S. Patents.

**Gregory P. Crawford** became dean of the College of Science and professor of physics at the University of Notre Dame in 2008. He was previously professor of engineering and physics (1996–2008) and dean of engineering (2006–2008) at Brown University. He joined Brown University in 1996 after working at the Xerox Palo Alto Research Center (PARC) as a member of the research staff. His research focuses on soft matter materials, photonic materials, medical devices, displays, nano-science, magnetic resonance, and photonic devices. The creative deployment of his basic research has resulted in two biotechnology start-up companies, Myomics, Inc. and Corum Medical, Inc., and his inventions have been licensed to companies. During the 2003–2004 academic year, Dean Crawford was on sabbatical at the Technical University of Eindhoven in the Netherlands, working on the underlying physics of novel phenomena of patterned liquid crystals and polymers with potential use in displays and security applications. In the summer of 1999, he was a visiting scientist professor at the Philips Research Laboratory (Natlab) in Eindhoven, working on the physics and applications of emissive and lasing materials. Dean Crawford holds 18 U.S. patents and has authored and coauthored more than 300 research and education publications

including review articles and book chapters, and is the editor of a number of books: *Liquid Crystals in Complex Geometries formed by Polymer and Porous Networks* (Taylor & Francis, 1996); *Flexible Flat Panel Displays; Liquid Crystals; Frontiers in Biomedical Applications* (World Scientific, 2007); and *Cross-Linked Liquid Crystalline Systems: From Rigid Polymer Networks to Elastomers* (this contribution). He also served as editor of a special edition on nanotechnology in displays and medical displays for the *Journal for the Society for Information Display*. He is a fellow of the Society for Information Display. Dean Crawford's teaching interests include optics, photonics, waves, soft matter, and high technology entrepreneurship at both the undergraduate and graduate levels.

**Slobodan Žumer** received his BSc and PhD (1973) from the University of Ljubljana. During 1975–1976 he held a postdoctoral position at the Université libre de Bruxelles and later during 1984–1986 he held a visiting position at the Liquid Crystal Institute of KSU. In 1987 he became professor of physics at the University of Ljubljana and in 1986 the Scientific Counselor at the Jozef Stefan Institute. His teaching interests include statistical physics, thermodynamics, optics, and soft matter physics at both the undergraduate and graduate level. He served as a head of the physics department (1997–1999) and as a dean of the Faculty of Mathematics and Physics (2005–2007) at the University of Ljubljana. In 2008 he started his four-year term as a president of the International Liquid Crystal Society. His research interests are theory, modeling, and simulations of soft matter with particular stress on liquid crystals, polymer-dispersed liquid crystals, liquid crystalline elastomers, and colloidal dispersions. He is the head of the Research Group for Physics of Soft and Partially Ordered Matter at the University of Ljubljana and the head of the Research Group Physics of Soft Matter, Surfaces, and Nanostructures at Jozef Stefan Institute. Professor Žumer with coworkers has published more than 200 research publications including review articles and book chapters that were cited more than 5000 times. He is a coauthor of three U.S. Patents, and coeditor of four books (*Liquid Crystals in Complex Geometries: Formed by Polymer and Porous Network*, Taylor & Francis, 1996; *Defects in Liquid Crystals: Computer Simulations, Theory and Experiments*, Kluwer, 2001; *Computer Simulations of Liquid Crystals and Polymers*, Kluwer, 2005; *Novel NMR and EPR Techniques*, Springer, 2006). During the period 2001–2007 he was a member of the editorial board of the *European Physical Journal E* and currently a member of the editorial board of *Liquid Crystals*. He is a fellow of the IOP and a member of APS.

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# *Part I*

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## *Densely Cross-Linked Systems*

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# 1 Densely Cross-Linked Liquid Crystal Networks by Controlled Photopolymerization of Ordered Liquid Crystal Monomers

## *Properties and Applications*

*Johan Lub and Dirk J. Broer*

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## 1.1 INTRODUCTION

Polymers with a controlled molecular organization in all three dimensions are of interest because of their unusual, but very accurately adjustable and addressable optical, electrical, and mechanical properties. An established method to produce 3-D ordered polymers is the photoinitiated polymerization of liquid crystal (LC) monomers [1–4]. The variety in possible LC phases of low-molar-mass reactive mesogens provides diversity in the choice of the type of the molecular order, all being accessible to be fixed by the polymerization process [5–8]. Known techniques to establish monolithic molecular order in LCs, such as rubbed surfaces, surfactant-treated surfaces, external electric, or magnetic fields or flow, can be applied or even can be combined with each other to create films of even more complex molecular architectures [9]. The molecular structure of LC monomers can be tailored, for example, to optimize on the mechanical and optical properties of the films. Furthermore, blends of monomers can be made to adjust the properties in the monomeric state, such as the LC transition temperatures and the flow viscosity, and in the polymeric state, such as the elastic modulus, the glass transition ( $T_g$ ) temperature, and the refractive indices.

When polyfunctional (more than one polymerizable group) LC monomers are polymerized in the bulk, the so-called LC networks are produced which, especially at higher cross-link densities, exhibit a stable molecular organization up to the degradation temperature of the polymers. In that sense they distinguish themselves from a class of LC networks that in literature normally is denoted as LC elastomers, often siloxane based, by the absence of phase transitions and the much higher moduli at room temperature. The history of densely cross-linked LC networks goes back to the end of the 1960s where different authors suggested polymerizing and cross-linking LCs in their mesophase aiming highly ordered polymers [10,11]. Thermally initiated bulk polymerization (thermosetting) of LC diacrylates was reported to yield three-dimensionally cross-linked polymer networks with a strong optical anisotropy and the molecular order of the frozen-in monomer phase was retained to the decomposition temperature [12–15]. However, the use of high temperatures to initiate the polymerization often conflicts with the temperatures at which the LC phases of many of the reactive LCs appear. During heating to, and processing in, the LC phase the polymerization starts prematurely before the desired monolithic orientation is established and defects become permanently frozen-in. It is for this reason that photoinitiation is highly preferable for the bulk polymerization and network formation. In the presence of small amounts of polymerization inhibitors, typically of the order of 100 ppm, the monomers can be processed at elevated temperatures until the desired LC phase and long-range order has been obtained. As soon as the desired molecular order has been established in the monomer it can be rapidly fixed by exiting a dissolved photoinitiator, which normally has a concentration between 0.05 and 5 wt% depending on the application and sample thickness, with actinic light of an appropriate wavelength, mostly around 360 nm.

The first reports on the bulk photopolymerization of reactive LCs were on monoacrylates forming linear LC side-chain polymers [16–20]. Real fixation of the molecular order in this case often does not occur and the formed polymer still exhibits various mesophases and can be heated to an isotropic state, although the transition

temperatures differ from those of the initial monomer. Consequently, phase transitions might also occur during the polymerization process with a change of order, type, and degree, as a result. In addition phase separation might take place if the LC state of the polymer does not mix with that of the initial monomer, which results in defects in the aimed monolithic order. It is for this particular reason that the bulk photopolymerization of polyfunctional LC monomers (photosetting LCs) became so important. For instance, the photoinitiated free-radical polymerization of monolithically ordered nematic LC diacrylates produces a stable polymer with the same texture as observed for the monomer and almost the same degree of molecular order [1–3]. But also the use of LC diepoxides [21,22], LC divinylethers [23–26], and LC dioxetanes [27] polymerized by photocationic mechanisms essentially lead to the same results.

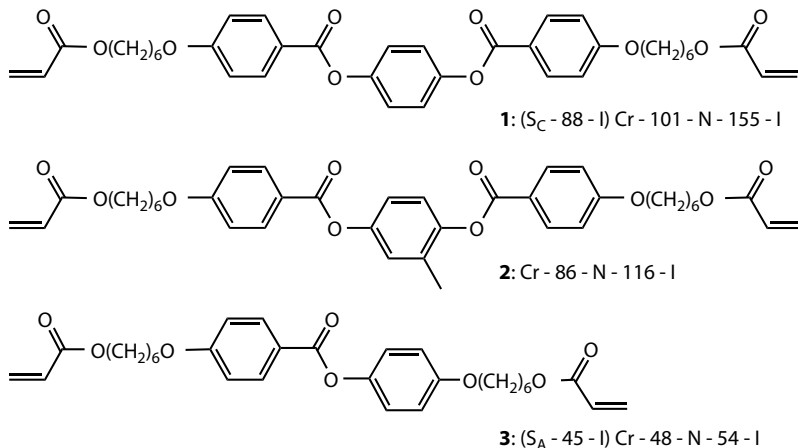
The optical properties of thin films of monolithically ordered LC networks are quite similar to those of the low-molar-mass LCs. They are transparent for light in the visible wavelength region, exhibit a high birefringence up to 0.25 at 589 nm [3], are able to show selective reflection in the case of a cholesteric order [6,8], and exhibit a half-wave optical retardation in the case of a twisted nematic molecular arrangement [5,28]. These properties make the materials ultimately suitable for the creation of various optical devices as polarizing beam splitters, organic Wollaston prisms, retardation films, color and infrared filters, and so on. All the properties are temperature insensitive and stable against environmental (light, humidity, temperature) aging. The mechanical properties are, apart from their anisotropic nature, of the same class as those of the isotropic acrylate and epoxide networks meaning that the modulus and strength are of the same order and depend strongly on the molecular parameters like cross-link density and the ratio between stiff and flexible units [29]. An interesting mechanical feature is that due to a unidirectional or planar molecular order the thermal expansion can be brought back to essentially zero into one or two directions. This implies that built-up of thermal stresses are avoided when the networks are applied as coating or encapsulate on an inorganic substrate [30].

This chapter will discuss structure–property relationships of the LC monomers and their polymers. By means of some of their applications and the desired properties we will demonstrate further how the properties can be tuned further by the combination of molecular design, alignment technology, polymerization conditions, and eventual additional photochemistry.

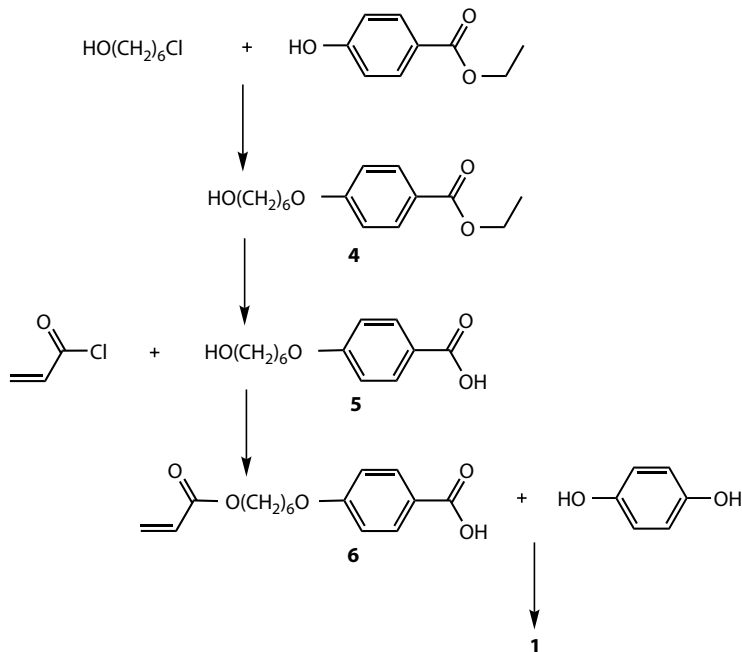
## 1.2 NEMATIC NETWORKS

### 1.2.1 STRUCTURE PROPERTY RELATIONSHIP IN NEMATIC (DI) ACRYLATES

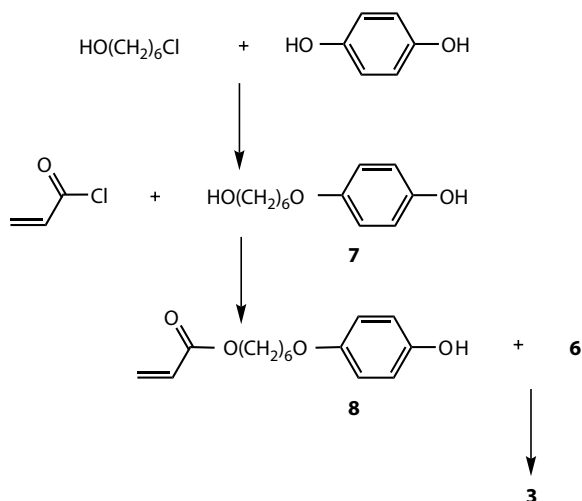
Figure 1.1 shows the structure of diacrylate **1** that we prepared more than 20 years ago. It is, as most LC monomers appeared to be, crystalline at room temperature. Upon heating it melts at 108°C and becomes nematic up to 155°C [1]. During supercooling, a monotropic smectic-C phase is observed below 88°C before it crystallizes again. The synthetic steps to make this molecule are outlined in Figure 1.2. The intermediate ethyl ester **4** is normally not isolated. In comparison with a similar molecule with the same aromatic core but with two hexyloxy end groups [31], the presence of the acrylate moiety hardly changed the crystalline melting temperature but destabilized



**FIGURE 1.1** Structure and phase transitions of 1,4-phenylene bis(4-(6-acryloyloxyhexyloxy)benzoate) **1**, 2-methyl-1,4-phenylene bis(4-(6-acryloyloxyhexyloxy)benzoate) **2**, and 4-(6-acryloyloxyhexyloxy)phenyl 4-(6-acryloyloxyhexyloxy)benzoate **3**. (Cr = crystalline, N = nematic phase, S<sub>C</sub> = smectic-C phase, I = isotropic phase.)



**FIGURE 1.2** Synthesis of 1,4-phenylene bis(4-(6-acryloyloxyhexyloxy)benzoate) **1** (see Figure 1.1).



**FIGURE 1.3** Synthesis of 4-(6-acryloyloxyhexyloxy)phenyl 4-(6-acryloyloxyhexyloxy)benzoate **3** (see Figure 1.1).

both the nematic and the smectic phase by reducing these phase transitions with  $50^\circ\text{C}$  and  $32^\circ\text{C}$ , respectively. The relatively high melting point of **1** allows only processing at elevated temperatures. In order to lower the processing temperature, as well as to modulate the properties of the polymer films of interest for their applications, several chemical adaptations were carried out to the structure of this compound. These adaptations include changes to the central mesogenic group, to the spacer, to the polymerizable group, and of course to combinations of these.

Upon substitution of one of the hydrogen atoms of the central ring of **1** by a methyl group, large changes in thermal transitions were observed. Synthesis of these molecules proceeds very similar; during one of the synthetic steps in Figure 1.2 hydroquinone was replaced by the commercial available methyl hydroquinone [32]. This compound **2** exhibits a melting point  $22^\circ\text{C}$  lower and an isotropic transition  $39^\circ\text{C}$  lower than that of **1**. Moreover, the influence of such a methyl group on the ordering results in complete disappearance of the monotropic transition to the smectic-C phase observed in **1**. Monomer **2** crystallizes extremely slow compared to **1**, which makes it possible to process it in the supercooled nematic phase at moderate temperatures. Mixtures of this compound with other compounds (e.g., other reactive LCs) can be more crystallization resistant and are therefore, very well suited for processing at room temperature (e.g., after spincoating from a solution) to form highly aligned films that can subsequently be photopolymerized. Also, other liquid crystalline diacrylates derived from several hydroquinones have been described [33].

Other mesogenic groups have been studied as central group for nematic liquid crystalline diacrylates. Compound **3** (Figure 1.1) shows a smaller mesogenic group. It exhibits only a very small nematic phase. Its synthesis is described in Figure 1.3. Monoalkylated intermediate **7** is easily separated from the di-alkylated product [34]. Conditions were found to form the acrylate group in **8** without the reaction of the