Liquid Crystalline Polymers

History of Liquid Crystalline Polymers

The liquid crystalline (LC) state was first observed by Austrian botanist and chemist F. Reinitzer more than a century ago, and it was then confirmed in 1888 by German physicist O. Lehmann who named such a state of matter as “liquid crystal” in 1900. While low molecular mass (LMM) liquid crystals were successfully used in LC displays (LCDs), the development of LC polymers (LCPs) followed an independent path. Conceptually, LCPs are prepared with the incorporation of mesogenic groups that are responsible for the formation of LC mesophases, such as rod-like (calamitic) and discotic ones, into polymer chains. Depending on where the mesogens are attached, traditionally there are three major categories of LCPs. Main-chain LCPs (MCLCPs) have mesogens in the polymer backbone, while mesogens of side-chain LCPs (SCLCPs) are incorporated as side groups in a polymer with a relatively flexible main chain. In main-chain/side-chain combined LCPs (MCSCLCPs), mesogens are in both the backbone and side chains. Other classes of LCPs include mesogen-jacketed LCPs (MJLCPs), dendronized LCPs, and LC networks (LCNs).

Almost right after the emergence of the polymer concept proposed by H. Staudinger in 1921, D. Vorländer quickly realized in 1923 that LCPs must exist after studying LMM LCs for more than two decades. With the consideration of his early pursuit of the concept of MCLCP, D. Vorländer can be regarded as the father of polymeric LCs. The first LC phase exhibited by polymers was reported in 1937 by F. C. Bawden and N. W. Pirie from a solution of a tobacco mosaic virus (a lyotropic phase). Meanwhile, the first LC phase from a synthetic polymer was found in a lyotropic solution of poly(γ -benzyl-L-glutamate) (PBLG). In 1956 C. Robinson identified that the phase of this α -helical polypeptide was similar to those of LMM cholesteric LCs. D. G. H. Ballard made PBLG fibers from the lyotropic phase in 1958, but they were not commercialized. S. L. Kwolek and coworkers at DuPont synthesized a wholly aromatic polyamide (a lyotropic LCP) in 1965. It was later commercialized as KevlarTM by the company. Polymers processed in the LC state were expected to maintain the anisotropy in the solid state and should exhibit excellent strength in the direction of orientation. Indeed, the results proved that KevlarTM fibers have outstanding tensile and other properties. This is another milestone in the LC history. Nowadays, KevlarTM fibers are used in various applications, such as radial tires, brake linings, bulletproof vests and composites, to substitute steel, fiberglass, etc.

In contrast to lyotropic LCs that show a mesophase in a solution, thermotropic LCs form a mesophase upon tem-

perature changes. W. J. Jackson and coworkers at Eastman-Kodak made a vital contribution to the development of thermotropic MCLCPs. They synthesized rigid, random copolymers of aromatic polyesters in the 1970s. Afterwards, syntheses of many LCPs with excellent mechanical properties were realized. And the LCPs have been exploited in various application areas. Commercialized products include X7GTM (Eastman-Kodak) and VectraTM (Celanese). These thermotropic MCLCPs have the advantages from both the LC and the conventional thermoplastic states, including melt processability and high mechanical properties as well as excellent thermal and chemical stability.

From the beginning, the main driving force for developing SCLCPs was aimed to incorporate them into displays owing to their seemingly attractive advantages in processing and applications. However, early synthetic attempts mostly failed in that the synthesized polymers were not liquid crystalline. The key development of SCLCPs was realized by H. Ringsdorf, H. Finkelmann, and coworkers in 1978. They proposed to insert a flexible spacer between the side-chain mesogen and the backbone, so as to decouple the motions of the flexible main chain and the LC side chains. Only after that, were systematic studies on SCLCPs possible. These polymers show different nematic, smectic, and cholesteric LC phases depending on mesogens and polymer main chains. Unfortunately, no commercial LCDs based on SCLCPs are available because of a great disadvantage that the time constants are lengthened. Nevertheless, SCLCPs can be quite useful as functional materials, such as responsive materials and soft actuators.

LCNs are cross-linked LC materials with locked-in arrangement of the molecules. Their unique optical properties allow the preparation of thin films to enhance the performance of a display. In the meanwhile, LC elastomers (LCEs) are a relatively new type of LC materials. P. G. de Gennes first proposed these materials in 1975, and H. Finkelmann *et al.* synthesized and demonstrated the fascinating functions of LCEs in 1981. LCEs are potentially useful as electromechanical actuators (e.g., artificial muscle) and tunable cholesteric lasers.

From the theoretical point of view, L. Onsager first introduced an LCP theory by using a virial expansion in 1949. He explained the lyotropic behavior of rigid molecules. In 1956, P. J. Flory adapted his lattice model of polymers to rigid rods and predicted the polymer/solvent phase diagram that was determined experimentally by C. Robinson. Then W. Maier and A. Saupe incorporated their mean-field theory into the Flory lattice model in 1959 and 1960.

Major Developments during the Past 40 Years

In contrast to the decoupling concept, the first MJLCs proposed by Q. Zhou and coworkers in 1987 had a very short flexible spacer or even no spacer inserted between the rod-like mesogenic side group and the backbone. The “jacketing” effect (or the steric effect) of the bulky side groups forces the backbone to stretch, resulting in a semi-rigid rod-like polymer chain, *i.e.*, the side chain and the main chain are coupled together. The rigidity of MJLC was predicted in the first MJLC publication and later proved experimentally. Thus, the physical properties of MJLCs are similar to those of MLCs, although chemically they are more like SLCs. Furthermore, unlike conventional MLCs and SLCs, the whole polymer chain serves as a supramolecular rod-like mesogen to form columnar mesophases. Therefore, more rigid MJLCs exhibit lyotropic behaviors. Because of this “jacketing” effect, even non-mesogenic side groups are used to construct MJLCs, as long as there is strong enough steric hindrance. In addition, when there are special interactions, such as π - π stacking, between the side groups, the MJLC polymer chain behaves like a supramolecular tablet that can form smectic phases. X. Wan, E. Chen, X. Fan, and Z. Shen also contributed a lot in the molecular design, synthesis, and structural determination as well as structure-property relationship investigation on MJLCs.

Almost at the same time, V. Percec developed dendronized LCPs by attaching mini-dendrons in the side chains. Similar to MJLCs, these polymers also have strong steric hinderance between the side chains. They can also behave like supramolecular rods to form columnar phases. The molecular shapes of dendronized LCPs differ when different shapes of dendrons are used. For cone-shaped dendrons, V. Percec and G. Ungar found that the polymer will form a core-shell sphere and assemble into sphere-forming structures, including Frank-Kasper A15 phase.

In the 1980s, B. Reck and H. Ringsdorf *et al.* first synthesized MCSLCs merely out of a scientific curiosity. In many conventional MCSLCs, both main-chain and side-chain mesogens are oriented in the same direction. Recently, H. Zhang, E. Chen and coworkers found that MCSLCs composed of MJLC main chains can exhibit biaxial orientation.

As one of the important and active areas in the LC field, there are many exciting developments in LCN and LCE materials reported by H. Finkelmann, R. Zentel, P. Keller, M. H. Li, and others. H. Finkelmann realized photo-controlled deformation (a large contraction of 20%) in a cross-linked LCP system containing azobenzene moiety in 2001. Subsequently, T. Ikeda first observed the bending/unbending behavior in polydomain and monodomain films of LCEs. Recently, Y. L. Yu succeeded in the light-controlled transportation of liquids in an LCE tube.

Recently, Y. Ji and E. M. Terentjev *et al.* incorporated dynamic covalent chemistry into cross-linked LCPs to obtain a so-called “LC vitrimer” (LCV) with a shape memory effect. Y. Zhao and coworkers combined the dynamic covalent bond with azobenzene mesogens, leading to an LCV that can be easily reprocessed and programmed by UV irradi-

ation. D. J. Broer and C. N. Bowman *et al.* achieved “photoinduced plasticity”, in which light and heat can activate the relaxation of the stress in the elastic cross-linked LCP and the LC-isotropic phase transition, respectively.

Molecule-crosslinked LCPs (mc-LCPs) are prepared by cross-linking self-assembled small molecules, forming free-standing films. T. Kato *et al.* developed mc-LCPs with vertical or planar columns by modified surface or shearing followed by photopolymerization under UV irradiation. C. O. Osuji *et al.* and T. Kato *et al.* also used other orientation methods for the alignment of columns, including soft surface confinement method, magnetic field, and hydrogen bonding.

In the development of other functional LCP materials, H. Yang and coworkers developed a unique LC composite system with the coexistence of polymer-dispersed and polymer-stabilized liquid crystals. The light transmittance of the film can be reversibly controlled by temperature change. Recently, they realized ultra-wide broadband reflection in an LC composite film of a polymer-stabilized cholesteric LC system by introducing thiol-acrylate chemistry. With the introduction of tetraphenylethylene units into the polymer backbone, Z. Yu and B. Tang *et al.* obtained a fluorescent MLC with aggregation-induced emission (AIE) property.

As for the progress of theories, X. Wang and M. Warner developed a mean-field theory for LCPs. The theory successfully predicted the phase behaviors of main-chain polymers with alternating rigid and flexible units and SLCs. The theory of M. Warner, K. P. Gelling, and T. A. Vilgis proposed in 1988 is vitally important in the understanding of LCEs. It correlates the mechanical properties of the elastomer with microscopic molecular parameters.

In the more physical aspects, S. Z. D. Cheng identified highly ordered smectic phases in polyester-based MLCs. A kind of interesting SLC, hemiphasmidic SLC (with hemiphasmid-type dendrons) was first studied by H. Ringsdorf and V. Percec *et al.* Recently, E. Chen *et al.* found that the supramolecular column of some hemiphasmidic SLCs contains multiple chains. In this multi-chain model, a polymer chain bundle serves as the columnar core. Such multi-chain columns can serve as strong physical cross-linking, rendering materials with excellent shape memory effect. And D. Chen *et al.* discussed the superlattices in SLCs with discotic mesogens. C. K. Ober, C. Y. Li, Q. Zhou, Z. Shen, and others systematically investigated hierarchical structures of block copolymers (BCPs) containing MJLC segments. H. Yu successfully realized photo-induced alignment and large-scale ordering of LC BCPs by taking advantage of the supramolecular cooperative motions between the microphase-separated nanostructure and the LC phase.

Prospect of Future

In the future, LCPs may continue to find niche applications where their unique properties and advantages can be beneficial. For instance, with increasing demand of LCP materials having low dielectric constant and low dielectric loss, new MLCs may be commercialized for 5G-related applications. Electroluminescent MLCs may be

processed into oriented systems with polarized emission. Side-chain materials may also possess such optical properties with appropriate self-assembled structures. More smart and soft actuator systems are expected from further development of LCEs. With the consideration of responses of LCPs to a variety of stimuli, such as electric and magnetic fields, heat, light, and mechanical forces, these actuators based on orthogonal responsive systems would become even “smarter”. The utilization of dynamic covalent bonds in cross-linked LCPs would offer reversible alignment and recyclability. There are still many challenges in this field, such as the design of new types of molecular structures and the deep understanding of the physics of LCPs. It is even more important than before for scientists in different disciplines to cooperate to further promote the advance of LCP science and technology. As noted by X. Wang and Q. Zhou in the 2004 book, “LC polymers are expected to have an even brighter future.”

Zhi-Hao Shen
Peking University

Qi-Feng Zhou
Peking University

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The views expressed in this editorial are those of the author.