# LIQUID CRYSTALLINE POLYMERS, MAIN-CHAIN

## Introduction

The liquid crystallinity of low molecular weight liquid crystals (LMWLCs) was found more than 100 years ago, when Reinitzer synthesized several esters of cholesterol. In the liquid crystalline (LC) state, the substance shows characteristics of a liquid in terms of its mobility, while it exhibits characteristics of a crystalline material in terms of its optical properties because of the anisotropy in the structure (1,2).

After more than two decades of research work on LMWLCs, Vorländer, in 1923, realized that liquid crystalline polymers (LCPs) must exist too (3,4). The first reference to a polymeric mesophase was in 1937 when Bawden and Pirie found that a solution of tobacco mosaic virus formed two phases, one of which was birefringent in certain concentrations (4). The first liquid crystalline phase for a synthetic polymer was a solution of  $poly(\gamma$ -benzyl-l-glutamate), reported by Elliot and Ambrose in 1950 (5). A few years later, Flory, based on the lattice model, proposed his well-known theory in treatment of liquid crystallinity in lyotropic systems (6). Flory proposed to divide the molecule into several submolecules, usually called segments, which consists of rigid rod-like moieties. Using this model, he concluded that molecular structure and geometry were the most important factors to induce liquid crystallinity. According to the Flory theory, a state with partial order can be formed above a critical concentration whereas the orientations of molecules are totally random below the critical concentration. The transition from a random to a partial order state is discontinuous. During the phase transition, isotropic phase and anisotropic phase coexist (7). The predicted critical axial ratio for the phase transition is 6.4 in a nonsolvent system (7). Flory later incorporated

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the temperature effect into the lattice model. For LMWLCs, the aspect ratio is defined as L/d, in which L is the length and d is the diameter of the molecule. For LCPs, the aspect ratio is replaced by the persistence ratio by substituting the molecule length L by the persistence length q.

The revelation of the theory to form the LC phase and the discovery of LC properties from rigid-chain polymers occurred coincidently, which led to an extensive search for new kinds of rigid-chain LCPs from academia and industry. DuPont scientists led the invention and successfully synthesized and identified lyotropic LCPs made of rigid wholly aromatic polyamides in the 1960s and later commercialized the high performance fiber under the name Kevlar (8,9). This became an important milestone in the development of LCPs. Since then, many LCPs with excellent mechanical properties have been synthesized and their applications in various areas have been explored. Workers at Carborundum in the early 1970s patented an aromatic copolyester based on a biphenol monomer and later used the trade name as Ekkcel I-2000 to test market (10,11). This material was diagnosed to possess LC characteristics several years after the invention. Eastman Kodak reported the first well-characterized thermotropic aromatic-aliphatic copolyesters by the reaction of *p*-acetoxybenzoic acid (ABA) and poly(ethylene terephthalate) (PET), later tested market under the trademark X7G (12–14). Both Ekkcel and X7G failed in commercialization because the former had to be processed at extremely high temperatures, whereas the later had too much PET which lowered the performance. Celanese developed various tractable wholly aromatic thermotropic polyesters and poly(ester-amide)s with the trademark Vectra in early 1980s, based on composition reported in patents and elsewhere (15, 16). Early development of Vectra LCP aimed at fiber applications, and the unique applications in electrical and electronic interconnection devices were serendipitously discovered and developed in the 1980s. Today, Kelvar fibers have replaced steel, fiber glass, asbestos, and graphite for varieties of applications, including radial tires, brake linings, and composites. Vectra LCP series of resins have been molded for electronic, telecommunication, medical, and other applications. Extruded and blown films are used for strength members and print circuit board, respectively (5.17).

Thermotropic main-chain LCPs have unique combination of properties from both LC and conventional thermoplastic states; these include melt processibility, high mechanical properties, low moisture take-up, and excellent thermal and chemical resistance. With the successful development of these LCPs and recognition of their unique properties, comprehensive research and development have been carried out by both academia and industry (3,5,9,11,14,16–26). Among various R&D directions, the synthesis of new LCPs (3,14,16,17,19–22,24,26), their rheology behavior (27–31), morphology, compatibility and processing of LCPs and blends (32–34) have received most attention.

### Synthesis of Main-Chain LCPs

Polyesters and poly(ester-amide)s are two important series of main-chain LCPs. In general, poly(ester-amide)s show increased thermal stability compared to polyesters (5,9,16). They both are synthesized by polycondensation reactions. In

order to increase the reactivity, monomers usually have to be acetylated *in situ* or before conducting the polycondensation reaction (5,9,16). Using the synthesis of LC polyester as an example, the synthesis procedure is described as follows. The transesterification reactions start with phenyl esters of diacids with acetylated aryl diols at relatively high temperatures. Normally, the reaction temperature is higher than the highest melting point of monomers. In order to reduce oxidation, the polymerization is commonly conducted in a nitrogen atmosphere. When low melt viscosity oligomers are obtained, the melt becomes turbid since the fluctuations of orientation of the mesogenic domains are in the range of the wavelength of visible light. A vacuum is then applied to the reaction system to further remove the by-products from the melt and to increase molecular weights. In order to facilitate the diffusion process, a stainless high-torque steel stirrer is desirable to improve the mixing and to accelerate the evolution of by-products, such as acetic acid. A multistep change in the temperature profile is the key to facilitate the molecular weight enhancement. The polymerization reaction can be carried out with or without a catalyst. Catalysts may affect the color and the thermal stability of the final product (18,35). In the reported kinetics study of bulk LCP polycondensation (36–38), for example, the ABA/2,6-acetoxynaphthoic acid (ANA) reaction system, the kinetics was investigated by titrimetry of evolved acetic acid trapped in a sodium hydroxide solution or monitoring the volume of acetic acid. It was found the polycondensation obeyed second-order kinetics irrespective of whether the reaction was catalyzed or uncatalyzed. A Similar conclusion was found for thin-film polymerizations (35).

Most monomers for LCP syntheses are highly crystalline, but do not have characteristics of liquid crystallinity (16,20–22,24–26). During the polymerization, an LC phase forms, and the LC texture evolves with the progress of polymerization and further annealing. To study the in situ morphological evolution of LCPs and annihilation of liquid crystal textures (or defects) during polymerization reactions, a powerful and convenient technique has been developed using the heatstage polarizing microscope (39,40). This novel approach modernizes the previous film polymerization technique (41–44) and has been extended to investigate the reaction kinetics, effects of catalysts, and monomer structures on the formation of various main-chain LC polyesters and poly(ester-amide)s (35,45,46) as well as to study the evolution of surface energy of LCPs during the polymerization reactions (47). Figure 1 shows a typical evolution of polymerization for 73/27 ABA/ANA with a thickness of 10  $\mu$ m at 230°C. After the monomer crystals melt and the reaction system reaches the proposed temperature, the reaction system becomes a homogenous phase as shown in Figure 1 (500 s). In the early stage of polycondensation reaction, oligomers form in the molten monomer phase. Their molecular weights and chain lengths increase with reaction time. When the chain lengths of oligomers reach a certain value, they form the LC phase and separate from the isotropic melt. Figure 1 (515 s) shows the reaction-induced phase-separation process during polymerization. The dark area in the micrographs is the isotropic phase; the bright area represents the LC phase. The first sign of forming the LC phase is that many bright LC domains instantaneously appear in the view range. Because of the polydispersity of the chain length, oligomers are partitioned within the isotropic and LC phases according to their chain lengths. A fraction with relatively longer chain lengths forms LC domains, while others remain in the isotropic



**Fig. 1.** Micrographs showing morphologies of 73/27 ABA/ANA polymerization reaction system at different reaction times. All the micrographs were obtained from the same area of the same sample. Reaction temperature: 230°C.

phase (39). After the appearance of LC phase, the sizes of LC domains quickly increase, and correspondingly the number of domains decreases because of domain growth and coalescence of adjacent LC domains. As a result, the total view area becomes an anisotropic LC phase (950 s).

LCPs exhibit a variety of textures of different length scales, originated from flow and deformation. A frequently observed texture called *banded texture or stripe texture* often emerges in the samples in which relaxation or shrinkage of molecular chains occurs. The conditions inducing this texture include the following: subjecting to shear and/or elongation flow (48), evaporating the solvent from a lyotropic LC (49,50), and quenching a thermotropic LC from a high temperature (51). As a consequence of stress relaxation after shear or volume deficiency induced by solvent evaporating or quenching, banded texture appears but the local order does not decrease significantly. In the 73/27 ABA/ANA reaction system, with the increase in molecular weight, the volume deficiency causes the appearance of banded texture since adhesion to the substrate prevents uniform shrinkage in three dimensions. Figure 1 (240 min) shows banded texture in the late reaction stage. However, the banded texture may not appear in some other compositions and reaction temperatures. For example, in some cases, the crystallization occurs and interrupts the formation of banded texture (39).

**Modification of Main-Chain LCPs.** Modifications of main-chain LCPs suitable for conventional processing equipment, without compromising the uniqueness of LC characteristics and the superior mechanical properties, have received most attention. Low cost LCPs are also in high demand. Most frequently used methods include synthesizing by random copolymerization, introducing kinks into the polymer chains by using meta or ortho linkages, introducing flexible linkages, and incorporating bulky side groups into the polymer chains (5,9,16–18,20–22).

**Random Copolymerization.** Random copolymerization is an effective way to disturb the regular structure of the polymer chain. The lack of periodicity along the chain inhibits crystallization, and thus reduces the crystallinity and depresses  $T_{\rm m}$  (the transition temperature to form an LC phase), without necessarily leading to an additional loss of mesogenicity and  $T_{\rm i}$  (the transition temperature

from an LC phase to an isotropic phase). This approach has been adapted when designing random copolymers such as Vectra A by Celanese (Ticona) with commercial success. Vectra A is a copolyester based on ABA and ANA with a mole ratio of 73/27. The melting point of this LCP is around 280°C, which is much lower than the melting points of either ABA or ANA homopolymers (5,16,18).

The morphologies of both ABA and ANA homopolymers and 73/27 ABA/ANA copolymer prepared by thin-film polymerization show that crystallization occurs in the homopolymerization systems and the liquid crystal state remains stable in the copolymerization system (39–44), clearly indicating that the random copolymerization is an effective way to retard the crystallization. Transmission electron microscopy revealed that the microstructures of homopolymers of ABA and ANA had more obvious lamellar texture (41–44).



**Introduction of Kinks.** Introduction of kinks into the polymer backbone effectively reduces the regularity of the molecules, and thus lowers the melting temperature. However, the incorporation of kinking units has an unfavorable influence on the liquid crystallinity since the kinks disrupt the straightness of the molecules. Also, the inducing of kinks into molecular chains is unfavorable for the thermal stability of the LCPs (16–26). The exact role of kinks has attracted remarkable attention because the formation of liquid crystallinity is not directly related to the kink content and many interesting phenomena have been found. For example, *m*-acetoxybenzoic acid (mABA) has a kink created by the meta linkage. However, the thin-film polymerization results of mABA/ANA indicate that the LC phase may still be observed even when the mABA content is as high as 66 mol% at  $183^{\circ}C$  (44).



Isophthalic acid (IA) is a monomer extensively employed to modify LCPs because its cost is low and the meta linkage can induce a kink into the molecular chain. The resultant polymer has a lower  $T_{\rm m}$ . However, the meta linkage also has a detrimental effect on the stability of the LC phase because it will disturb the LC character if its percentage is too high. In the thin-film polymerization of ABA/acetoxy acetanilide (AAA)/IA system, the critical meta-linked IA content is 26 mol% at 280°C, which means the liquid crystal phase can only be formed when IA content is lower than 26% and crystallization occurs once the IA content is higher than this critical point (45).

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Phthalic acid (PA) has an ortho linkage which can also introduce a kink into the molecular chain. However, it is seldom utilized to modify the LCPs because the liquid crystal phases are not stable for the systems containing PA units (46). Recently, it was found that, in the early stage of thin-film polymerization, both ANA/AAA/PA and ANA/AAA/IA systems form liquid crystal phase when the PA or IA content is 20%. However, with the further reaction going on, the ANA/AAA/PA system crystallizes, whereas the ANA/AAA/IA system remains in the LC state (46).



Since kinks shorten the persistence length of the polymer chain, the LC characteristics may be destabilized if the kink content is high. Figure 2 shows the critical ANA content for the two reaction systems, ANA/AAA/IA and ANA/AAA/PA, to form liquid crystallinity at different reaction temperatures. For the ANA/AAA/PA system, the window of reaction temperature is wide because of the low melting point  $(205^{\circ}C)$  of PA, and the critical ANA content range is very



**Fig. 2.** The dependence of the critical ANA content for ANA/AAA/PA and ANA/AAA/IA systems on reaction temperature. ■ ANA/AAA/IA system; ▲ ANA/AAA/PA system.

narrow for all the temperatures we investigated. For the ANA/AAA/IA system, the reaction temperature window is restricted by the high melting point ( $342^{\circ}$ C) of IA. When conducting the polymerizations at low temperatures, such as  $250^{\circ}$ C, the reactions are incomplete and IA crystals remain after reaction. So the reaction temperatures used have to be relatively high, from 280 to  $360^{\circ}$ C. The most striking and interesting phenomenon in Figure 2 is that PA has a much higher tendency to form liquid crystallinity than IA. One of the causes may be due to the *cis* conformation of the bridging groups, especially for the amide group, which can compensate for the  $60^{\circ}$  angular conformation induced by an ortho linkage. As a result, the reaction system containing PA may have more opportunities to form a relatively straight conformation than the system containing IA. The other possibility is that the resultant polymer in the ANA/AAA/PA system may form a spiral chain conformation because of the rotation of the bridging groups, thus inducing liquid crystallinity (46).

The final morphology of LCPs depends on kinks content because the elastic constants of LC during the reaction are strongly affected by the kink structure. During polymerization, the defects in the LC phase involve very high distortion energy in the case of rigid or semirigid polymers. Disclinations with opposite signs tend to attract each other in order to release the energy and lead to the annihilation and the decrease in the number of defects (52–55). Because the elastic constant values decrease with increasing kink content, the defect density increases with increasing kink content since LCPs with kinks cannot annihilate fast and completely in the reaction system (45,46).

**Modification with Flexible Segments.** Modification with flexible segments is another important way to improve the melt processibility. By inserting flexible segments to separate the mesogenic units along the polymer chain, the chemical periodicity of the molecule is preserved. These polymer systems are referred to as semirigid polymers. The influence of flexible linkages on the melting temperature can be considered in several ways. In addition to facilitate the motion of the polymer chain, the random distribution of monomeric units also decreases the melting temperature further if the flexible segments are introduced by a copolymerization. The disadvantages of introducing a flexible spacer to a polymer chain are that it disturbs the liquid crystallinity and affects the thermal stability of the resultant polymer.

The most typical spacer segments used consist of flexible polymethylene  $-(CH_2)_n$  of varying length n.  $T_i$  decreases in a zigzag fashion in homologous series in which the spacer length regularly increases. This zigzag characteristic is referred to the odd-even effect.  $T_i$  tends to be higher when there is an even number n of methylene groups in the spacer, but this oscillation is attenuated on ascending the series. This effect is best understood by assuming the conformation of the methylene spacer to be all trans, which has the lowest energy. An even-numbered polymethylene spacer possesses a set of low energy *trans* conformers that force the rigid units to adopt a collinear disposition. In contrast, an odd-numbered spacer places the two mesogenic groups in the angled orientation disfavoring the ordering of a nematic phase (19).

**Introduction of Lateral Groups.** Lateral groups have been introduced to lower the melting points of LCPs. Grafting bulky side groups onto the polymer main chain influences the melting temperature in several ways. It effectively

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increases the interchain distance and reduces the interchain forces so that the efficiency of the chain packing is reduced. Moreover, this effect is much enhanced by the copolymerization because the randomness of the polymer chain further decreases the crystallinity and melting point (19,23). Unfortunately, the lateral group has a strongly unfavorable effect on the formation of liquid crystallinity, especially for the bulky lateral groups, which will immediately cause the loss of liquid crystallinity if they are randomly distributed in the molecular chain. Two reaction systems ANA/AAA/3-fluorophthalic acid (FPA) and ABA/AAA/PA were compared to identify the effect of lateral group on liquid crystallinity. Because of the kink structure of the PA unit and the different sizes of hydrogen and fluorine atoms affect the formation of crystallinity, the critical ABA content to form the LC phase for the ABA/AAA/FPA and ABA/AAA/PA systems at 280°C are 9 and 5%, respectively, indicating that fluorine atoms modify chain distance and conformation and lower the stability of the LC phase (56).



Rigid-chain polymers containing different concentration of laterally attached side rods have been demonstrated in bulk reactions using a Vectra LCP as the base material, as illustrated in Figure 3 (57). These polymers exhibit liquid crystallinity even up to a maximum side-rod concentration of 20 mol%. The crystallinity of the



Fig. 3. Incorporation of laterally attached side rods.

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polymers, however, decreases with the increase in the side-rod concentration. The advantage of these polymers is their lower dielectric constants compared with their parent polymers, ie, similar polymers but without laterally attached side rods. A dielectric constant of 2.6 can be achieved by incorporating 10 mol% of laterally attached side rods, which is 0.5 lower than that of its parent polymer. The reduction in dielectric constant may be attributed to low crystallinity and less dense packing structure of the polymers induced by incorporating of laterally attached side rods. This series of polymers also has good thermal stability (see also LIQUID CRYSTALLINE POLYMERS, SIDE-CHAIN).

## Thermal Stability and Degradation

Thermal stability, degradation behavior, and kinetics of commercially available main-chain LC polyesters such as Ticona's Vectra, BP-Amoco's Xydar, DuPont's Zenite, Eastman's X7G, and Mitsui's LC polyimide have been reported (58–62). There are two degradation processes for most of these LCPs in air, but only one in N<sub>2</sub>. By observing the ftir bands, it can be concluded that CO<sub>2</sub> is the dominant product in both N<sub>2</sub> and air, and it exists all through the degradation process. In air, the by-products may consist of H<sub>2</sub>O, CO, CO<sub>2</sub>, phenols, aryl esters, ketones, and others through dehydration, decarboxylation, and decarbonylation. The stability at the beginning of the decomposition process follows the order Xydar SRT-900 > Vectra A950 > Vectra B950 (60). The activation energy  $E_a$  of thermal degradation for Vectra A950 and Vectra B950 are about 232 and 197 kJ/mol in N<sub>2</sub>, and 222 and 159 kJ/mol in air, respectively (60).

## Crystallization

Crystallization of main-chain LCPs is considerably different from that of conventional polymers, such as polyethylene or PET. LCPs have reduced flexibility compared to the latter, which implies that large translations of their molecules are required for recrystallization. Thus the crystallization process in an LC phase may present its own peculiarities. The orientational order associated with mesophase may act as a precursor for further crystal growth, especially in monotropic LCPs where the metastability of mesophase generally leads to the formation of a more stable crystal phase.

The overall crystallization process includes two steps, primary nucleation followed by crystal growth. The process can be well described by the Avrami equation (63,64) as shown:

$$1 - \theta = \exp(-Kt^n)$$

where  $\theta$  is the relative crystallinity at time t, n is the dimensionality of crystal growth, and K is a temperature-dependent constant that depends on the growth geometry, the number of nuclei present, and the linear growth rate of polymer crystals. For most LCPs, n is found to be less than 1 for the growth of liquid crystallinity.

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The crystallization process for most commercially available LCPs can be found elsewhere (65–72). For most LCPs, there are two transition processes: one is a fast transition process, ascribed to the aggregation of rigid chains, and the other is a slow transition process developing gradually during the later heattreatment stage. These two processes also manifest in different crystal structures. For LCPs synthesized from ABA/ANA compositions, the fast process leads to hexagonal packing with cylindrical symmetry along the chain direction, while the slow process gives rise to orthorhombic packing (66). The Avrami parameter nvalues for Vectra A are in the low range 0.2–0.5, which is due to the fact that each crystal does not grow with a constant radial growth rate (70). The crystallization and phase transition behavior in LC polyimides have been investigated (73–78). Smectic-layered structures have been found for some polyimides.

## Surface Energy

The surface energies of Vectra A, Vectra B, and Xydar have been reported using contact angle techniques at room temperature (79,80). Experimental data suggest that surface energy values match between the two-liquid geometric method (81,82) and the three-liquid acid–base (83,84) method if a correct combination of testing liquids is used. However, three-liquid Lifshitz–van der Waals acid–base method is more suitable for the surface energy calculation of these three LCPs, and provides much more information, eg, acidity and basicity of LCP surfaces. The average surface energies of Vectra A-950, Vectra B-950, and Xydar are 41.0, 41.9, and 42.3 mJ/cm<sup>2</sup>, respectively. In addition, all these three LCPs should be classed as monopolar Lewis bases because their Lewis acid components,  $\gamma^+$ , are negligible. The incorporation of a small amount of  $-C(CF_3)_2$ — in the main chain can lower LCP's surface energy and the fluorocarbons are preferentially enriched at the air–polymer interface (85).

## Morphology and Microstructure

In the LC phase and within a volume element, the molecules are aligned along one common direction in average, labeled by a unit vector  $\mathbf{n}$ . A region within the sample volume where the directon does not change very much is defined as a *domain*. The distribution of domain orientations within the sample forms texture (86,87). The various rheological behaviors, which strongly affect the processing conditions and final properties of these materials, are the results due to the interaction between the texture and the flow field. To sum up, the final properties are determined to a large extent by the microstructure, which, in turn, is due to a combination of the inherent properties of the LCPs and the flow conditions during processing.

It has been reported that three kinds of distinct fibrils could be observed in oriented LCP fibers, extrudates, and mold parts; they are 50-nm microfibrils, 500-nm fibrils and 5  $\mu$ m macrofibrils (88). For highly oriented fine fibers, the LC domains are elongated along the fiber direction with a size of about 500 nm in the transverse direction. A periodic and inherent defect layer of about 50 nm has also been noticed in the fiber structure. For large diameter extruded rods, the degree of orientation decreases from the outer skin to the core because the shear rate is higher at the outer skin than at the core (89). Increasing the draw ratio cannot eliminate the skin-core structure. However, by changing the temperature profile within the extrusion die, one may be able to induce a higher shear rate at the core and thus enhance the overall degree of orientation and fiber modulus (90). The mechanical properties of extruded LCP films in various directions follow typical macromolecular composites theory and can be predicted using the Tsai–Hill equation (91). Because of the complexity of flow patterns during the injection molding, a layered structure can be found in the cross-section of molded parts (5,16,88). Each layer corresponds to each flow pattern. However, the degree of orientation decreases as one proceeds from the skin to the core (88). Later studies revealed much detailed morphology of the nature of the microfibrillar hierarchy and the shape of the microfibrils was found to be tape-like (92, 93).

## LCP Rheology and Blends

Since the main characteristic of thermotropic LCP melts is the persistence of order in the material even when the stresses causing deformation are removed, the rheological behavior of LCP is different from normal polymers. The viscosity vs shear rate behavior for LCPs can be represented by three distinct regions: (1) a shear thinning region at low shear rates, (2) a Newtonian region in an intermediate shear rate region, (3) a power-law shear thinning region at high shear rates (27). Although very few sets of data show all the three regions in a single polymer, analysis of the published data of a number of authors for LCPs identified the three flow regions (28). An important characteristic of LCPs is that they have longer relaxation times compared with flexible coil polymers. Two relaxation times for LCP melts one for the stresses and the other for orientation have been reported (29). Although these phenomena were related through the stress-optical law for conventional flexible coil polymers, they were independent for LCPs. The relaxation time of orientation was longer than the relaxation time of stress; thus, the orientation LCPs achieved during processing was retained in the solid state more easily than for flexible chain polymers.

Using the unique and superior properties of LCPs to enhance the thermal and mechanical performance of various engineering resins, studies have been conducted since late 1980s (94–104). The LCP phase is preferentially oriented in the direction of flow. LCPs can also be viewed as a processing aid (lubricant), which effectively reduces the viscosity of the blends if the LCP content is low (32,94,96–99). It is found that the LCP domains do not always deform into fibrils as reinforced elements for some LCP/thermoplastic blends. One must provide adequate shear stress and torque history to deform LCPs into elongated fibrils. The rule of thumb is to have process conditions which yield the viscosity ratio of the dispersed LCP phase to the thermoplastic matrix to be lower than 1 (99,103). LCPs blends also suffer from poor adhesion strength between the LCP phase and the thermoplastic matrix. Forming cross-linkable LCP blends is one of the ways to overcome it (105-107). LCP/LCP blends have also been developed (33,108) to yield LCPs with a better performance.

## Applications of Main-Chain LCPs

Thermotropic LCPs have a great potential as structural materials. They have high strength and stiffness in the direction of the molecular alignment and their low melt viscosity and low shrinkage facilitate processing. Most applications of mainchain LCPs are based on the excellent mechanical properties of these materials (3,5,9,16,17,26,30). As we know, high modulus and high tensile strength occur when polymer molecules are aligned and extended. In ordinary isotropic polymers, the molecules tend to align and to uncoil in tensile and shear fields, but recoil and partially lose their orientation when removing the stress. To obtain high modulus, there are the following requisites: the individual molecule should be stiff, the alignment of the molecules has to be nearly prefect, and ratio of the aromatic to aliphatic linkages must be high. These conditions are satisfied by wholly aromatic LCPs because of their high tendency to align and to remain in that orientation. The chemical structures of wholly aromatic LCPs provide a good answer for these attainments.

Because thermotropic wholly aromatic LCPs have characteristics such as high strength, low melt viscosity, low shrinkage, ease of processibility, excellent thermal resistance, low water, and gas absorption, they have wide applications in following areas: fibers, rods, sheets, composites used in mechanical and chemical industries; chip carriers, connectors, switches used in electronics; connectors, couplers, buffers used in fiber optics; interior components, brackets in aerospace; and so on (3,5,9,16,17,26,30).

LCP fibers have high strength and stiffness and are lightweight. Fabrics of LCP fibers (such as Vectran fibers) have been used as ballistic garments, helmets, and military flak jackets. Excellent cut/tear resistance and thermal insulation also make LCP fibers desirable for protective gloves and clothing. Sheet products made from mineral-filled LCP variants or multilayer copper and LCP laminates have been used for thermoforming and electroplating for printed circuit board. Large-diameter melt-extruded LCP rods have been used to replace steel wire and even used as strength members in optical cable applications. This is because LCP rods have the following characteristics: lightweight and flexible, excellent tensile properties, which prevent optical fibers from breaking during the lay down process. very small negative coefficient of thermal expansion, which minimize the external stress, good chemical resistance, and almost zero water regain. LCP rivets offer an attractive alternative to metal for fasteners without the high cost and heavy weight of titanium or the corrosion problem associated with aluminum. Because Kevlar and Vectran fibers are strong, nonabrasive, dimensionally and thermally stable, they also have been used to reinforce brake linings. For injection-molding resins, the addition of fillers or fiber-reinforced elements into neat LCP resins may be the best approach to obtain high quality. Most commercial LCP products contain 30-70% fillers or fiber-reinforced elements in order to lower the LCP cost and have balanced mechanical and electrical properties. LCPs offer at least a few advantages over other engineering resins in electric applications, for example, low mold shrinkage, fast cycling time, capability of molding thin parts, low moisture regain, and better chemical and mechanical properties. In addition, LCPs are little affected by radiation.

LCPs have been in commercial use for over 20 years, and new applications are still emerging. It is expected that commercial LCPs are still in the growth phase and that significant increases in usage will occur in the twenty-first century.

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