

Chapter 12

Combined Main-Chain/Side-Chain Liquid Crystalline Polymers: Synthesis and Supramolecular Ordering

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12.1 Introduction

The self-reproduction of complex molecules and supramolecular structures in living systems are realized by self-organization and genetic code transfer (Champe and Harvey 1994). Liquid crystalline polymers represent one of the most important macromolecular systems that have the capability of self-organization because of their unique molecular architectures with high anisotropy (Collings and Hird 1997). Although liquid crystalline order exists in many natural biomacromolecules, modern chemistry allows scientists to synthesize a new family of liquid crystalline polymers that mimic biological systems to construct synthetic functional systems with ordered structures. The most distinguished feature of liquid crystalline polymers lies in that they exhibit intermediate morphological states between crystalline (or glassy) and liquid states, where macromolecular chains can be self-organized into a wide spectrum of ordered structures such as nematic, smectic, and cholesteric mesophases (Donald and Windle 1992). Over the past decades, numerous endeavors have been made to rationally design and synthesize liquid crystalline polymers with controllable supramolecular structures.

Liquid crystalline polymers are basically built up from rigid molecular units, the so-called mesogens, which are linked by covalent bonds to construct macromolecular chains, while small molecules containing mesogens afford liquid crystals. Figure 12.1 gives the schematic representation of integrating liquid crystal molecules (or mesogens) into macromolecules to form main-chain liquid crystalline polymers (MCLCPs) in which mesogens are incorporated into the macromolecular backbone, side-chain liquid crystalline polymers (SCLCPs) in which mesogens are attached onto flexible polymer chains, and combined main-chain/side-chain liquid

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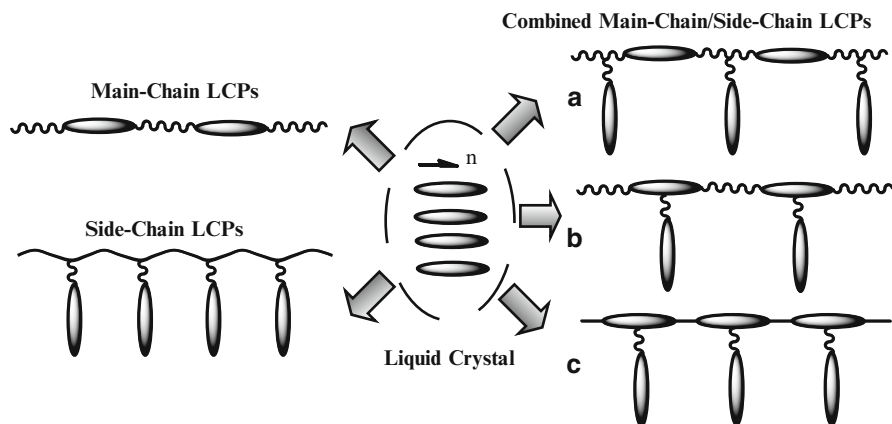


Fig. 12.1 Schematic representation of formation of main-chain liquid crystalline polymers (LCPs), side chain LCPs, and combined main-chain/side-chain LCPs with side-chain mesogens attached onto (a) main-chain flexible spacers, (b) main-chain mesogens having flexible spacers, and (c) rigid-rod main-chain LCP

crystalline polymers (MCSCCLCPs) consisted of a main-chain liquid crystalline backbone and side-chain mesogenic groups. The main-chain backbone of MCSCCLCPs may be either semi-rigid (Fig. 12.1a, b) or rigid (Fig. 12.1c) (Zentel and Brehmer 1996). As far as MCSCCLCPs are concerned, side-chain mesogens may be attached via flexible spacers onto main-chain flexible spacers or onto main-chain mesogens with or without flexible spacers. There are various terminal groups like $-\text{CN}$ and $-\text{OCH}_3$ that terminal groups of side-chain mesogenic moieties. If liquid crystalline polymers (LCPs) show ordered mesophases when they are heated to a certain temperature, they are called thermotropic LCPs, while lyotropic LCPs primarily depends on the concentration in a specific solvent to form mesophases.

Over 30 years ago the pioneering work of Reck and Ringsdorf (1985) gave great momentum to the synthesis of MCSCCLCPs, which opened the door to a whole variety of MCSCCLCP materials with a wide range of structural designs and synthetic methods. Ever since, intensive research efforts have been made to gain fundamental understanding of versatile supramolecular structures of MCSCCLCPs and their relationship with various properties of these polymers. Thus far, through molecular design, a couple of strategies have been applied to synthesize MCSCCLCPs. A number of research groups synthesized MCSCCLCPs by condensation polymerization (Zentel and Brehmer 1996) and free radical polymerization (Xie et al. 2010), while some research groups synthesized MCSCCLCPs by functionalization of biomolecules (Wu et al. 2003). Specific interactions were also demonstrated to be an effective approach for synthesizing MCSCCLCPs (Huang and Han 2006).

In particular, MCSCCLCPs have attracted much attention from academic interests in the study of the interplay between chemical structure and supramolecular

ordering. Emphasis has been placed on the investigation of influencing factors and their mutual effects on phase transition behaviors, which encompass the rigidity of main-chain backbone, attachment position onto either main-chain flexible spacer or mesogenic units, length of flexible spacer, molecular weight, and mesogen-grafting density (Xie et al. 2010, 2011; Huang and Shi 2012; Yang et al. 2012; Zhu et al. 2012; Wen et al. 2013). In turn, a variety of mesophases were observed because of the overall orientational order originating from interactions between main-chain and side-chain mesogens. The aim of this chapter is to give an overview of the chemistry of novel MCSCLCPs with an emphasis on current trends in synthetic methods, molecular design, supramolecular arrangements, properties, and applications.

12.2 Synthesis of Combined Main-Chain/Side-Chain Liquid Crystalline Polymers

To date, many synthetic strategies have been developed to synthesize MCSCLCPs due to the advancement of modern organic and polymer chemistry. Among these, synthetic methodologies such as condensation polymerization, free radical polymerization, atomic transfer radical polymerization, metathesis polymerization, polyaddition polymerization, grafting reactions, and self-assembly are extensively involved. The core mesogenic units in the main chain and side chain may be either identical or totally different, and representative mesogenic units include biphenylene, azobenzene, azoxybenzene, and *p*-phenylene benzoate. There are two ways to incorporate side-chain mesogens onto main-chain mesogens by either attaching side-chain mesogenic groups onto flexible spacers of a semi-flexible main-chain polymer or attaching side-chain mesogenic groups as lateral substituents onto mesogenic moieties of a semi-flexible or rigid-rod main-chain polymer.

12.2.1 Synthesis of Combined Main-Chain/Side-Chain Liquid Crystalline Polymers by Condensation Polymerization

12.2.1.1 Synthesis of MCSCLCPs with Side-Chain Mesogenic Units Attached onto Flexible Spacer Units of a Main-Chain Backbone

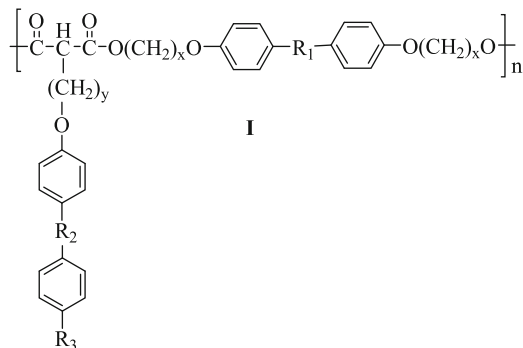
Condensation polymerization has been extensively used for achieving MCSCLCPs. The first example of combined MCSCLCPs (**I**) was synthesized by attaching side-chain mesogenic groups onto the flexible spacer of the main-chain backbone (Reck

Table 12.1 Phase transition temperatures of MCSCCLCPs with a chemical structure **I** (Reck and Ringsdorf 1985)

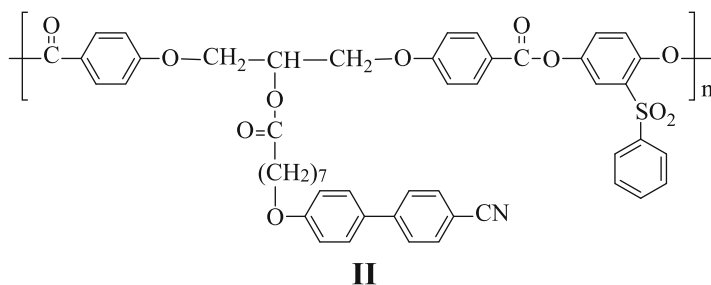
Sample No.	R ₁	R ₂	R ₃	x	y	Phase transition temperature (°C)
I-1	–	–N=N–	–OCH ₃	2	2	k 148s ₂ 176 i
I-2	–	–N=N–	–OCH ₃	2	6	k ₁ 124k ₂ 129 s _C 153 s _A 162 n 181 i
I-3	–	–N=N–	–OCH ₃	2	10	g 112k 162 (n 159) i
I-4	–	–N=N–	–CN	2	6	k ₁ 115k ₂ 140s ₂ 177 n 183 i
I-5	–	–N=N–	–OCH ₃	6	2	k ₁ 109k ₂ 120 n 153 i
I-6	–	–N=N–	–OCH ₃	6	6	k ₁ 108k ₂ 112 s _C 131 s _A 136 n 155 i
I-7	–	–N=N–	–OCH ₃	6	10	g 72s ₁ 120 s _C 139 s _A 154 i
I-8	–	–N=N–	–CN	6	6	g 61s ₁ 112s ₂ 184 i
I-9	–N=N–	–	–OCH ₃	2	6	k 112s ₂ 151 n 171 i
I-10	–N=N–	–	–OCH ₃	6	6	k 95 (s _C 90) n 152 i
I-11	–N=N–	–N=N–	–CN	2	6	g 53s ₂ 202 i
I-12	–N=N–	–N=N–	–CN	6	6	g 35s ₂ 189 i

Note: *g* glass transition temperature, *k* melting or solid-to-solid transition temperature, *s_A* smectic A, *s_C* smectic C, *s₁* unidentified ordered smectic mesophase, *s₂* unidentified disordered smectic mesophase, *n* nematic, *i* isotropic state

and Ringsdorf 1985). Specifically, these MCSCCLCPs were synthesized by melt polymerization at 200 °C between malonate monomers having side-chain mesogens and diols having main-chain mesogens using a catalyst system of diglyme and tetraisopropyl orthotitanate. As illustrated in Table 12.1, both nematic and smectic (*s_A* and *s_C*) mesophases were observed under optical microscope for these samples, and side-chain mesogens had broadened phase transition temperatures of their parental main-chain polymers. Furthermore, side-chain mesogens enhanced the stability of MCSCCLCPs, presumably due to interactions between main-chain mesogens and side-chain mesogens. This led the authors to hypothesize that side-chain mesogens were aligned parallel to main-chain mesogens.



Zhou and Han (2005) reported the synthesis of a MCSCLCP having a chemical structure **II**, which consisted of poly[(phenylsulfonyl)-*p*-phenylene-1,4-tetramethylenebis(4-oxybenzoate)] and a side-chain mesogen, 8-[(4-cyano-4'-phenyl)oxy]octanoic acid (7CNCOOH). This polymer was synthesized by condensation reaction between acid chloride monomer containing a side chain mesogen and a 1,4-biphenol monomer having phenylsulfonyl pendent group. This MCSCLCP exhibited a glass transition at 85 °C, and a nematic-to-isotropic (N–I) transition at 172 °C, which was 90 °C lower than that of the corresponding main-chain LCP. Thus, it was a glassy nematic LCP, arising from the bulky side-chain mesogen and pendent phenylsulfonyl group. As a result, lyotropic solutions with a concentration of 25–70 wt% in *o*-dichlorobenzene, *m*-dibromobenzene, or tetrachloroethane were successfully prepared from this particular LCP which allowed them to investigate rheological behaviors of lyotropic MCSCLCP and clarify one of the unresolved issues in LCP rheology, that is, the sign of first normal stress difference (N_1) in steady-state shear flow (Zhou and Han 2006). They demonstrated strong evidences of negative values of N_1 at intermediate shear rates for lyotropic solutions with concentrations up to ca. 27 wt%, which greatly supported theoretical predictions made by Marrucci and Maffettone (1989) and Larson (1990). In contrast, only positive values of first normal stress difference (N_1) in steady-state shear flow were observed in thermotropic states over the entire range of shear rates and temperatures investigated.



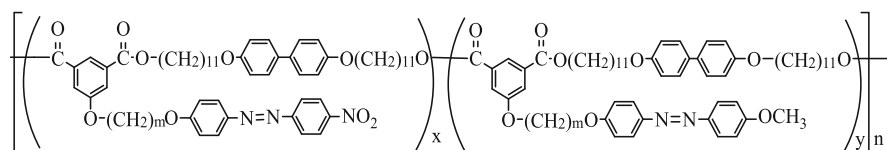
Another thermotropic MCSCLCPs (**III**) were synthesized by melt polymerization of isophthalate monomer and 11,11'-(4,4'-biphenylenedioxy)diundecanol using zinc acetate as a catalyst (Sato and Mizoi 2004; Sato et al. 2004). Isophthalate monomers contain nitro and methoxyazobenzene mesogenic units and three different aliphatic spacers (hexamethylene, octamethylene and decamethylene) in the side chain. As displayed in Table 12.2, homopolyisophthalates with the nitroazobenzene unit formed highly ordered smectic E mesophase, and those with methoxyazobenzene and their copolymers showed less ordered smectic B or smectic C mesophase. It should be pointed out that temperature ranges of smectic mesophases in copolymers showed a decreasing trend with increasing content of methoxyazobenzene. UV–vis spectra of the azobenzene-containing polymers exhibited absorption peak maxima both in solutions and in films. However, no

Table 12.2 Phase transition temperatures of MCSCLCPs with a chemical structure **III** (Sato and Mizoi 2004; Sato et al. 2004)

Sample no.	m	x/y ratio	Phase transition temperatures (°C)
III-1	6	1.0/0	k 68 s _E 143 i
III-2	6	0.8/0.2	g 40k 69 s _B 143 i
III-3	6	0.6/0.4	g 40k 72 s _B 141 i
III-4	6	0.5/0.5	g 43k 70 s _B 140 i
III-5	6	0.4/0.6	g 43k 73 s _B 140 i
III-6	6	0.2/0.8	g 40k 98 s _B 131 i
III-7	6	0/1	k ₁ 61k ₂ 108 s _C 133 i
III-8	8	1.0/0	k 77 s _E 141 i
III-9	8	0.8/0.2	k ₁ 68k ₂ 81 s _B 140 i
III-10	8	0.6/0.4	g 41k 84 s _B 140 i
III-11	8	0.5/0.5	g 43k 85 s _B 140 i
III-12	8	0.4/0.6	g 50k 86 s _B 139 i
III-13	8	0.2/0.8	g 51k ₁ 107k ₂ 123 s _B 137 i
III-14	8	0/1	g 60k 128 s _C 134 i
III-15	10	1.0/0	k 74 s _E 141 i
III-16	10	0.8/0.2	g 47k 87 s _B 140 i
III-17	10	0.6/0.4	g 47k 92 s _B 140 i
III-18	10	0.5/0.5	g 49k 91 s _B 140 i
III-19	10	0.4/0.6	g 54k 93 s _B 139 i
III-20	10	0.2/0.8	g 54k 91 s _B 135 i
III-21	10	0/1	g 53k ₁ 91k ₂ 101 s _B 133 i

Note: *g* glass transition temperature, *k* melting or solid-to-solid transition temperature, *s_B* and *s_E* are smectic B and smectic E, respectively, *i* isotropic state

fluorescent properties were observed, which might be attributed to the intra- and intermolecular quenching effects between electron-accepting nitro group and electron-donating methoxy group.

**III**

Because of unique features of chiral liquid crystalline polymers such as selective light reflection for cholesteric phase and ferroelectricity and fast switching times in electrical fields for chiral smectic C* phase (Zentel and Brehmer 1996), chiral mesogens have been introduced into MCSCLCPs (**IV**). These MCSCLCPs were prepared by melt polymerization of mesogenic malonates and mesogenic diols using tetraisopropyl orthotitanate as the catalyst at 140–150 °C (Kapitza and

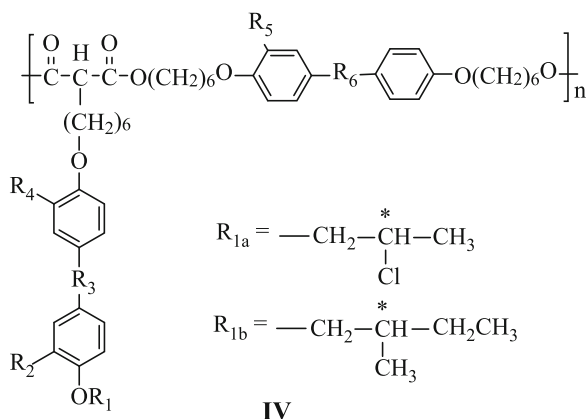
Table 12.3 Phase transition temperatures of MCSCLCPs with a chemical structure **IV** (Zentel and Brehmer 1996)

Sample no.	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	Phase transition temperature (°C)
IV-1	R_{1a}	H	H	Br	–	–	k 45 n* 111 i
IV-2	R_{1a}	H	H	H	–	–N=N–	k 109 s _C * 149 i
IV-3	R_{1a}	H	H	H	–	–N(O)= N–	k 57 s _C * 140 s _A 149 i
IV-4	R_{1b}	H	Br	Br	–	–	g 16s 37 i
IV-5	R_{1b}	H	Br	H	–	–N=N–	k 57 n* 88 i
IV-6	R_{1b}	H	Br	H	–	–N(O)= N–	g 12s 53 n* 91 i
IV-7	R_{1b}	H	Br	H	–	–	k 84 i
IV-8	R_{1b}	Br	H	Br	–N=N–	–	g 40 i
IV-9	R_{1b}	Br	H	H	–N=N–	–N=N–	g 38 i
IV-10	R_{1b}	Br	H	H	–N=N–	–N(O)= N–	g 41 i
IV-11	R_{1b}	Br	H	H	–N=N–	–	k 69 i
IV-12	R_{1b}	H	H	Br	–N(O)= N–	–	g 17 s 90 n* 96 i
IV-13	R_{1b}	H	H	H	–N(O)= N–	–N=N–	k 54 s _A 109 n* 141 i
IV-14	R_{1b}	H	H	H	–N(O)= N–	–N(O)= N–	g 20 s _A 108 n* 144 i
IV-15	R_{1b}	H	H	H	–N(O)= N–	–	k 77 s _C * 126 s _A 131 i
IV-16	R_{1b}	H	H	Br	–	–	k 59 s _C * 105 i
IV-17	R_{1b}	H	H	H	–	–N=N–	k 112 s _C * 129 n* 132 i
IV-18	R_{1b}	H	H	H	–	–N(O)= N–	k 63 s _C * 124 n* 133 i
IV-19	R_{1b}	H	H	H	–	–	k ₁ 151k ₂ 154 i
IV-20	R_{1b}	H	H	Br	–N=N–	–	k 56 s _C * 91 i
IV-21	R_{1b}	H	H	H	–N=N–	–N=N–	k 107 s _C * 111 n* 137 i
IV-22	R_{1b}	H	H	H	–N=N–	–N(O)= N–	k 53 s _C * 107 n* 138 i
IV-23	R_{1b}	H	H	H	–N=N–	–	k 130 s _C * 136 i

Note: *g* glass transition temperature, *k* melting or solid-to-solid transition temperature, *s_A* smectic A, *s_C** smectic C*, *n** cholesteric, *i* isotropic state

Zentel 1988). As indicated in Table 12.3, the dipole moment of –N(O)=N– was induced perpendicular to mesogenic groups, while other dipole moments were introduced by lateral substituents (e.g. R₁). As such, these polymers formed crystalline or highly ordered smectic phases at room temperature and showed cholesteric or chiral smectic mesophases at elevated temperatures. Lateral substituents not only decreased the melting temperature but also broadened mesophase transition temperatures. Dipole moments perpendicular to mesogenic groups or at the

chiral center facilitated high spontaneous polarisation in the chiral smectic C* phase (ferroelectricity).



Because of high temperature conditions required for the melt polymerization of chiral MCSCLCPs described above, judicious selection of chiral groups was necessary for preventing a racemization during the reaction. Later, a new synthetic route at room temperature was developed to address this issue (Kapitza and Zentel 1991). Specifically, precursor polymers with phenolic groups were first synthesized by the same melt polymerization process. Then, these precursor polymers with phenolic groups were reacted with chiral acid by esterification mechanism using a catalyst system of dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). The esterification yield was 90–100 %, affording 33 different chiral MCSCLCPs with cholesteric and chiral smectic C* mesophases.

12.2.1.2 Synthesis of MCSCLCPs with Side-Chain Mesogenic Units Attached onto Main-Chain Mesogenic Units

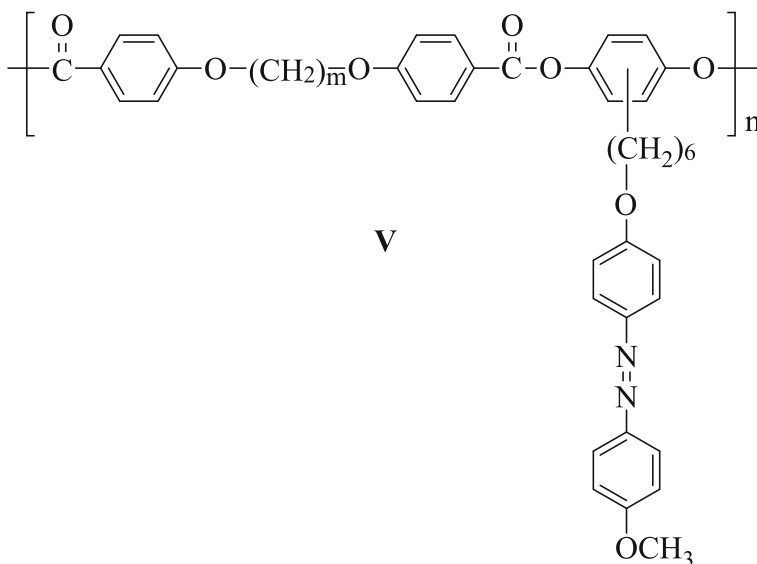
The other important family of MCSCLCP is referred to as those with side-chain mesogenic units as lateral substituents to a rigid rod polymer or to mesogenic units in semi-flexible main-chain LCPs. A series of combined MCSCLCPs (V) with side-chain mesogens attached onto main-chain mesogens were first reported by Reck and Ringdorf (1986). The design concept originated from lateral substituents in main-chain LCPs. The polymerization was accomplished by solution polymerization of hydroquinone monomers carrying a lateral mesogenic group and 4,4'-alkylenedioxydibenzoyl chlorides using tetrachloroethane as a solvent and pyridine as a catalyst. It can be seen from Table 12.4 that all polymers exhibited a glass transition temperature and a nematic-to-isotropic (N–I) transition temperature (>220 °C), while no crystallinity was observed for these polymers. The N–I

Table 12.4 Phase transition temperatures of MCSCLCPs with a chemical structure **V** (Reck and Ringsdorf 1986)

Sample no.	m	Phase transition temperature (°C)
V-1	2	g 90 n 310 i (decomposed)
V-2	6	g 56 n 268 i
V-3	9	g 45 n 221 i

Note: *g* glass transition temperature, *n* nematic phase, *i* isotropic state

transition temperature decreased with increasing length of flexible spacer in the main chain.



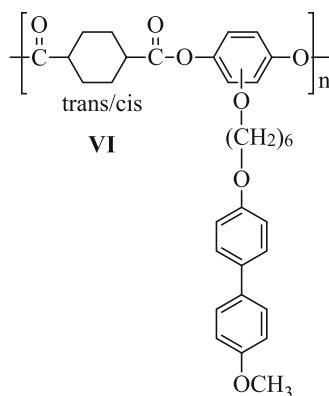
Rigid-rod main-chain LCPs have excellent mechanical properties but they are difficult to process because their clearing temperatures tend to be greater than their degradation temperatures. The lateral substitution of side-chain mesogens via a flexible spacer onto rigid rod main-chain LCPs is an effective way to reduce their clearing temperatures for practical applications. A series of MCSCLCPs were synthesized by melt polycondensation via transesterification reaction from *trans*-1,4-cyclohexanedicarboxylic acid, chloro-1,4-phenylene diacetate, and 6-(4-methoxy-4'-biphenyloxy)hexyl-1,4-phenylene diacetate (Reck et al. 1989). These MCSCLCPs combined both features of rigid-rod main-chain LCPs and of side-chain LCPs. The main-chain LCP, poly(chloro-1,4-phenylene-1,4-cyclohexanedicarboxylate), had a melting temperature of 309 °C. The introduction of small fraction (e.g. 10 mol%) of side-chain mesogenic groups significantly reduced the melting temperature to 240 °C, but the clearing temperature was still higher than 400 °C. When 100 mol% side-chain mesogenic monomers were used to polymerize with 1,4-cyclohexanedicarboxylate monomer, solution polymerization of acyl

Table 12.5 Phase transition temperatures of MCSCLCPs with a chemical structure **VI** (Reck et al. 1989)

Sample no.	Trans content (%)	Phase transition temperature (°C)
VI-1	97 ± 3	g 65k 183 n 337 i
VI-2	23 ± 3	g 60 i
VI-3	77 ± 3	g 64 n 212 i
VI-4	55 ± 3	g 57 n 130 i

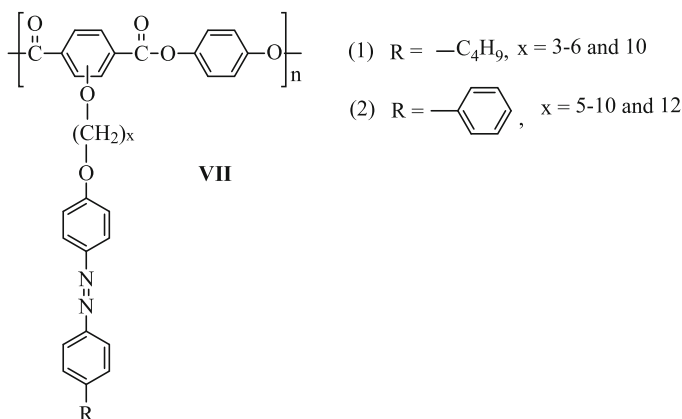
Note: g glass transition temperature, k melting temperature, n nematic phase, i isotropic state

chlorides and hydroquinone monomer containing side-chain mesogen was carried out using tetrachloroethane and pyridine as solvents. The thermal *trans-cis* isomerization occurred at temperatures above 250 °C, and thus the *cis*-contents could be achieved by thermal isomerization. The formed *cis*-units became a kink for disrupting the rigid rod main-chain structure, resulting in the reduction of clearing temperatures, as indicated in Table 12.5. However, in the case of excessive *cis*-contents (e.g. 77 %), the polymer became non-mesogenic as a result of only very few rod-like segments in the polymer backbone. This suggested that interactions between main-chain mesogens and side-chain mesogens in MCSCLCPs were a prerequisite for the formation of mesophase.



To understand the effect of flexible spacers on liquid crystalline properties of MCSCLCPs, Piao et al. (Piao et al. 1997) synthesized a series of MCSCLCPs (**VII**) carrying various lengths of oxypolymethyleneoxy spacers between a rigid-rod main-chain aromatic polyester and side-chain azobenzene mesogens by solution polymerization. It was borne out that shorter spacers ($x = 3-6$) favored the formation of nematic phases, whereas longer spacers ($x = 10$) favored the formation of biaxially oriented layered mesophases. The tentative hypothesis for this observation was that shorter spacers tended to prefer parallel orientation between a main-chain mesogenic backbone and pendent mesogenic groups through intramolecular interactions between them, leading to a nematic ordering in the melt. On the other hand,

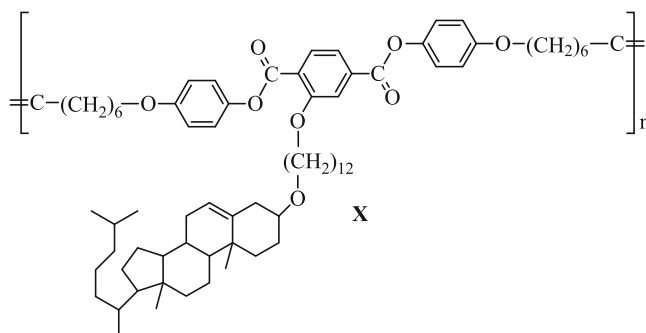
longer spacers would decouple interactions between main-chain and side-chain mesogens, resulting in the formation of a layered morphology in the melt. The other paper from the same group reported the substitution of n-butyl tail with phenyl group in order to increase the aromaticity or polarizability of side-chain mesogenic groups (Lee et al. 1999). It was anticipated to improve attractive interactions between main-chain and side-chain mesogens. As a result, all polymers formed nematic mesophases but not layered morphologies in melt, due to the parallel alignment of side-chain mesogens to main-chain mesogens. It should be mentioned that not only all these MCSCLCPs were semicrystalline, but also their clearing temperatures were higher than degradation temperatures.



Furthermore, Cha et al. (2001) reported the synthesis of MCSCLCPs (**VIII**) bearing pendant cholesterol moieties attached to the main-chain mesogenic backbone through oxyalkyleneoxy groups (hexamethylene, octamethylene, decamethylene, and dodecamethylene) of varying lengths. All these polymers were found to be amorphous due to the presence of irregularly placed bulky pendant cholesterol groups, but thermotropic. These polymers exhibited two thermal transitions before isotropization. The lower temperature transition occurred between 34 and 56 °C while the high-temperature one happened between 94 and 156 °C, both of which decreased with increasing spacer length. Noticeably, layered morphologies were formed in the mesophase especially for longer flexible spacers. The above observations demonstrated that the relative orientation of side-chain mesogenic units in MCSCLCPs with respect to their main-chain mesogens depended strongly on mutual interactions between the two structural elements. Consequently, the layered morphology was favorable if there was a great disparity in polarity between main-chain and side-chain mesogens, because side-chain mesogens would orient vertically to main-chain mesogens. The unique feature of biaxial orientation of MCSCLCPs has a great prospect in addressing the challenging issue existing in nematic LCPs, that is, the anisotropy in physical properties originating from the easy molecular orientation of nematic mesophase during processing.

12.2.2 *Synthesis of Combined Main-Chain/Side-Chain Liquid Crystalline Polymers by Acyclic Diene Metathesis Polymerization*

Acyclic diene metathesis polymerization (ADMET) proceeds in a step-growth manner with liberation of a gaseous ethylene side product. Joo et al. (2000) reported the use of ADMET for synthesizing main-chain, side-chain, and combined main-chain/side-chain liquid crystalline polyesters. The Grubbs' catalyst, bis(tricyclohexylphosphine)benzylideneruthenium dichloride, was employed and the reaction was conducted at 25–50 °C either in solution or bulk. The MCSCCLCP (**X**) was obtained from a diene monomer containing a built-in aromatic ester type mesogen bearing a cholesterol pendant via an oxydodecyloxy spacer. The advantage of this particular method lied in the fact that reasonably high molecular weight polymers could be prepared at a low temperature under very mild conditions. MCSCCLCP (**X**) had an average number molecular weight (M_n) of 53,200 with a polydispersity index of 2.9. Therefore, it was concluded that it was feasible to synthesize MCSCCLCPs containing functional side-chain groups without affecting the catalyst activity. MCSCCLCP (**X**) showed a glass transition temperature of 36 °C, a melting temperature of 68 °C, and a clearing temperature of 132 °C, and exhibited only polished marble textures for the nematic mesophase.



12.2.3 *Synthesis of Combined Main-Chain/Side-Chain Liquid Crystalline Polymers Based on Mesogen-Jacketed Liquid Crystalline Polymers*

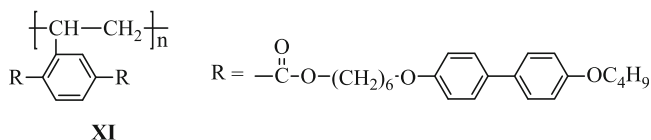
Mesogen-jacketed liquid crystalline polymers are a type of main-chain liquid crystalline polymers, which are not constructed by genuine mesogenic units in the main chain of polymers. As a matter of fact, bulky side groups that are crowded

around a flexible backbone force the flexible backbone to be rather extended and stiff by “jacketing” effect arising from the steric hindrance of pendent bulky groups (Zhou et al. 1987, 1989). As a consequence, these mesogen-jacketed liquid crystalline polymers exhibit liquid crystalline behaviors similar to the genuine main-chain LCs. As such, bulky pendent groups may pack parallel to one another to form columnar phase with two-dimensional long-range positional order, which may be considered as a molecular cylinder. It is worthy of noting that mesogen-jacketed liquid crystalline polymers are distinguished from conventional side-chain liquid crystalline polymers in that the absence of a flexible spacer between the flexible main-chain backbone and pendent side groups cause non-mesogenic side groups to fuse together to become a single conformational unit like a rigid rod. The question arises as to whether it is possible to synthesize mesogen-jacketed MCSCLCPs. When designing the polymer, the central rigid portion of the side chain should be attached to every second carbon atom along the backbone without a spacer might impose a great steric interaction on polyethylene backbone, resulting in a semi-rigid main chain; on the other hand, flexible spacers introduced in the side chain could facilitate mesophase formation of biphenyl moieties. Here, the function of vinyl monomer is twofold by providing strong “jacketing” effect to the backbone and forming liquid crystalline phases.

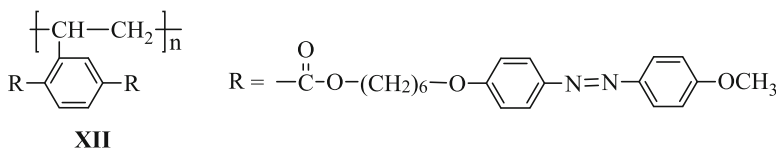
Xie et al. reported the first MCSCLCP (**XI**) with mesogen-jacketed liquid crystalline polymer rigid-rod main-chain and biphenyl as side-chain pendent groups by using atom transfer radical polymerization (ATRP) (Xie et al. 2008). Although the monomer containing side-chain mesogenic groups was rather bulky, ATRP method could be very effective in polymerization, affording polymers with well-controlled molecular weight and narrow molecular weight distribution. Differential scanning calorimetry (DSC) and optical microscope results revealed that phase behaviors of these polymers were rather complex with three different mesophases, which may be associated with the interplay between side-chain mesogens and main-chain jacketed mesogens of the polymer. Moreover, phase transition temperatures were also highly dependent on the molecular weight of the polymer, that is, higher molecular weight of the polymer led to higher phase transition temperatures.

Later, radical polymerization was used to prepare an MCSCLCP using the same monomer (Xie et al. 2010). Thermal transitions and hierarchical supramolecular ordering with biaxial orientation of this MCSCLCP were studied using differential scanning calorimetry, one- and two-dimensional wide-angle X-ray diffraction, and polarized light microscopy. Very recently, Wen et al.(2013) have synthesized a series of diblock copolymers composed of polystyrene and MCSCLCP (**XI**). Lamellar and rectangular cylinder morphologies were observed for these copolymers by small-angle X-ray scattering. As evidenced by differential scanning calorimetry and X-ray scattering results, MCSCLCP (**XI**) in the confined space of microphase separation was still able to exhibit its liquid crystalline structures with a rectangular main-chain scaffold on the nanometer scale and side-chain ordering on the subnanometer scale. Therefore, a three-length scale ordered

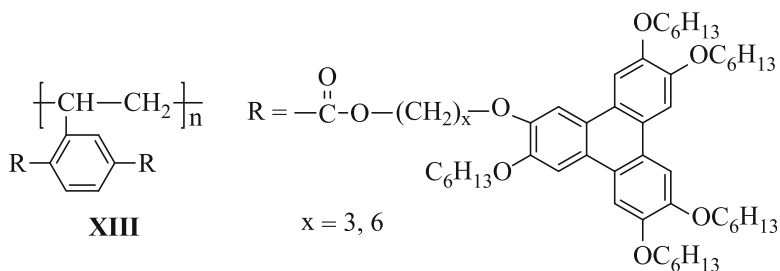
hierarchical structure could be observed in the same system, namely, microphase separation and double-length scale mesophase structure of the MCSCLCP.



Based on the same principle of molecular design, Xie et al. (2011) synthesized another MCSCLCP (XII) based on radical polymerization. Here, the side-chain mesogenic unit was azobenzene group. They confirmed that this MCSCLCP could form a hierarchically ordered structure with double orderings on both the nanometer and subnanometer length scales. The “jacketing” effect of pendent terephthalate side-chain to the polyethylene backbone constructed a two-dimensional centered rectangular scaffold. The packing of side-chain azobenzene mesogens inside the main-chain scaffold underwent the thermal transition from smectic B to smectic A, and then to isotropic. The confinement arising from the scaffold included the SmB-like packing and enhanced the stability of SmA-like structure. The hierarchically ordered structure rendered a biaxial orientation with side-chain mesogens perpendicular to main-chain mesogens. Upon UV irradiation, this MCSCLCP retained its liquid crystallinity even though azobenzene groups had been transformed into *cis*-conformation.



Interestingly, Zhu et al. (2012) introduced triphenylene units as side-chain mesogens for mesogen-jacketed MCSCLCPs. The polymer was synthesized through conventional free radical polymerization, and phase behaviors of these new MCSCLCPs were investigated. These MCSCLCPs exhibited excellent thermal stability. The attachment of discotic liquid crystals onto mesogen-jacketed liquid crystalline polymers had a significant effect on the liquid crystalline behavior of the polymer. These polymers formed rectangular columnar phases at relatively high temperatures. At low temperatures, triphenylene moieties in side chains formed a discotic nematic phase in conjunction with the columnar phase developed by rod-like supramolecular mesogens. For a longer flexible spacer, a higher symmetrical hexagonal columnar phase formed when the temperature exceeded 225 °C.

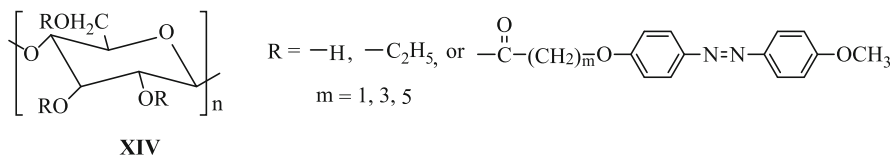


12.2.4 Synthesis of Combined Main-Chain/Side-Chain Liquid Crystalline Polymers Based on Biomacromolecules

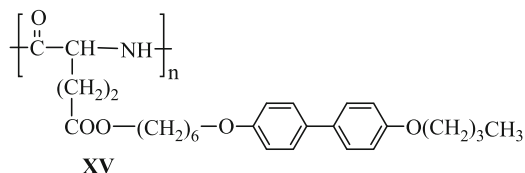
Cellulose is one of the most important biomacromolecules that can form cholesteric mesophases, and thus it can be regarded as a rigid rod main-chain LCP (Werbowyj and Gray 1976). The attachment of side-chain mesogens onto cellulose backbone via chemical bonds represents an alternative way to synthesize combined main-chain/side-chain liquid crystalline polymers. MCSCLCPs (XIV) were synthesized by coupling azobenzene-containing monomers having carboxylic acid end groups with ethyl cellulose. The esterification coupling reaction was enabled by using *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) as a catalyst in tetrahydrofuran (THF) solvent homogeneously (Hu et al. 2010). For MCSCLCP (XIV) with $m = 3$, thermal transition temperatures and phase structures depended on the degree of substitution (DS). At a low DS, the liquid crystallinity of the polymer was dominated by the ethyl cellulose backbone. When the DS increased, thermal transition temperatures and phase structures changed dramatically, arising from structural irregularities due to the asymmetrical substitution of mesogens.

In order to explore the relationship between spacer length and mesophase structure, a series of MCSCLCPs (XIV) with various spacer lengths were synthesized (Hu et al. 2010). The spacer length had also played an important role in the formation of liquid crystalline phases of these polymers. Glass transition temperatures, phase transition temperatures and the corresponding enthalpy of transitions decreased with increasing flexible spacer length. The mesophase structures of the polymer consisted of a large-scale ordered lamellar structure composed of ethyl cellulose main-chain mesogens and a relatively small-scale ordered structure formed by azobenzene side chains. All polymers formed a similar lamellar structure on a large scale. The small-scale ordered structure became relatively disordered, that is, from crystal ($m = 1$) to smectic B ($m = 3$) to smectic A ($m = 5$) at low temperatures. This was ascribed to interactions between the rod-like ethyl cellulose

main-chain and side groups, as well as the π - π stacking of azobenzene mesogens of these MCSCLCPs.

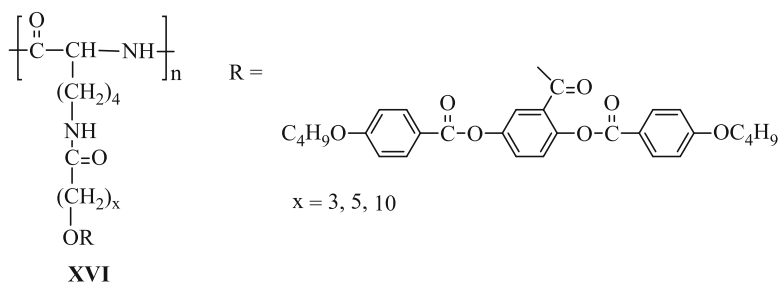


α -Helical polypeptides represent an important class of polymers that can form mesophase because of their rigid-rod shape. Watanabe and Tominaga (1993) synthesized a thermotropic MCSCLCP (XV) by linking a mesogenic biphenyl moiety to a mesogenic α -helical polypeptide with a flexible spacer. This MCSCLCP was prepared by an ester exchange reaction between poly(γ -methyl-L-glutamate) with 4-butoxy-4'-((ω -hydroxyhexyl)oxy)biphenyl in 1,2-dichloroethane using *p*-toluenesulfonic acid as a catalyst at 60 °C. This MCSCLCP had two thermal transition temperatures at 143 and 222 °C and correspondingly three distinct phases including crystalline, smectic A, and cholesteric phases. In the case of crystalline or smectic A phases, macromolecular chains constructed the characteristic layered structure in which α -helical main chains formed the layer while side-chain mesogenic groups were placed in the central part of layers with their long axes perpendicular to the layer. The cholesteric phase formed by main-chain α -helices occurred upon the collapse of the layered structure. These samples formed cholesteric liquid crystalline phases above the melting transition but formed layered structures at low temperatures driven by crystallization of side chains. The thermotropic transition behavior and mesophase structures were interpreted by the coupling effect of main-chain and side-chain mesogenic units.

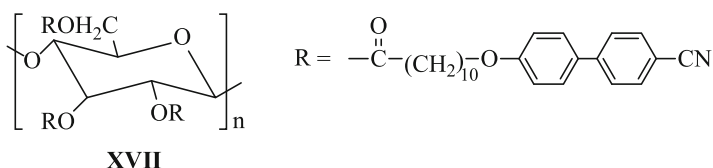


To obtain the coexistence of liquid crystalline ordering in both side-chain mesogens and main-chain rigid-rod polypeptide backbones, Schaefer et al. (2006) paved a new way to modify polypeptide by “side-on” approach, which facilitated the parallel orientation of side-chain mesogens with main-chain peptide backbones. Amino acid monomers with spacers of 3, 5, and 10 methylene units between lysine side chains and mesogens were first synthesized. Then, terminal acid groups of these mesogens were converted to *N*-hydroxylsuccinimide active esters that were subsequently coupled to ϵ -amino groups of $N\alpha$ -Z-L-lysine, yielding mesogen-derivatized lysines where the mesogen was coupled to the amino acid using a

robust amide linkage. The target MCSCLCPs were prepared by ring-opening polymerization using $(\text{PMe}_3)_4\text{Co}$ as an initiator in tetrahydrofuran solvent. The melting transition temperature and the degree of ordering of rodlike polypeptides in the liquid crystalline nematic state was finely tuned by varying the length of aliphatic linker between the polypeptide backbone and the mesogen. These MCSCLCPs displayed an unusual mesophase where both side-chain mesogenic group and polypeptide backbones formed ordered phases and coexisted in a nematic hexagonal structure. It was easy to draw fibers from the mesophase of these MCSCLCPs, indicative of good melt processability of this type of novel polypeptides.

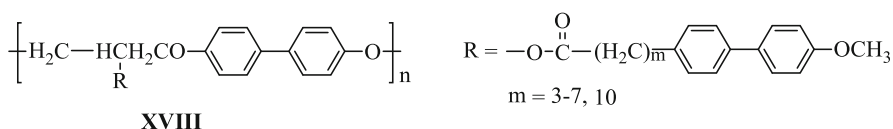


Although starch itself cannot form mesophase in thermotropic or lyotropic state, Huang et al. (Huang and Shi 2012) synthesized a thermotropic starch liquid crystalline polymer (**XVII**) by high-degree substitution (esterification) of hydroxyl groups on starch molecules with a mesogenic monomer, 11-(4'-cyano-biphenyl-4-yloxy)-undecanoic chloride, in the presence of pyridine. This unique starch-based liquid crystalline polymer might be also considered as a MCSCLCP. The long flexible spacer was judiciously selected for linking side-chain mesogens to the main-chain backbone, ensuring that the clearing temperature of this polymer would be less than its thermal degradation temperature. The elemental analysis showed that it had a degree of substitution of 2.68. This starch-based MCSCLCP exhibited a glass transition temperature of 29.6 °C and a nematic-to-isotropic transition temperature of 148.2 °C. Most interestingly, it showed a tensile strength of 37.9 ± 7 MPa and Young's modulus of 1.42 ± 0.14 GPa. This successful example may provoke the interest of engineering applications of starch.



12.2.5 Synthesis of Combined Main-Chain/Side-Chain Liquid Crystalline Polymers by Polyaddition

The polyaddition reaction between bis(epoxide) and “activated” diester was exploited by Chen et al. to synthesize MCSCLCPs (Chen et al. 1999). The first step of reaction was to synthesize six trimers with biphenyl mesogenic groups and polymethylene spacers. The second step of reaction was to polymerize these trimers and biphenol diglycidyl ether based on the addition reaction between epoxide and phenol ester functions. This polymerization was catalyzed by quaternary phosphonium chloride. It can be seen from Table 12.6 that there was a significant odd-even effect of the side-chain spacer not only on the thermal transition temperature but also on the crystallinity of MCSCLCPs. MCSCLCPs with even numbers of methylene units in the side-chain flexible spacer showed higher values of thermal transition temperatures and isotropization entropy. Specifically, all the MCSCLCPs were thermotropically nematic, although polymers with 3, 5 and 10 methylene units (*m*) in side-chain spacers were semicrystalline at room temperature, while other polymers were glassy.



12.2.6 Synthesis of Combined Main-Chain/Side-Chain Liquid Crystalline Polymers by Self-Assembly

Self assembly via specific interactions has been recognized as a powerful tool to construct a variety of supramolecular structures and has been turned out to be an intriguing pathway toward the synthesis of liquid crystals or liquid crystalline polymers (Kato and Frechet 1989a, b; Kato et al. 1999). Here, specific interactions

Table 12.6 Phase transition temperatures of MCSCLCPs with a chemical structure XVIII (Chen et al. 1999)

Sample no.	<i>m</i>	Phase transition temperature (°C)
XVIII-1	3	k 132.8 n 146.2 i
XVIII-2	4	g 73.1 n 156.1 i
XVIII-3	5	g 73.3k 99.5 n 127.3 i
XVIII-4	6	g 62.7 n 135.5 i
XVIII-5	7	g 55.1 n 118 i
XVIII-6	10	k 104.2 n 123.3 i

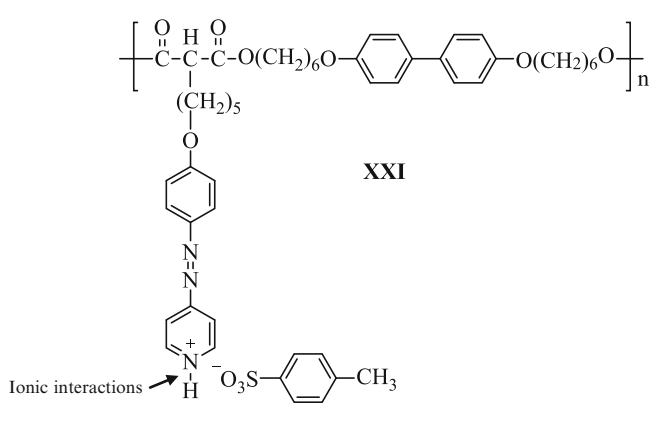
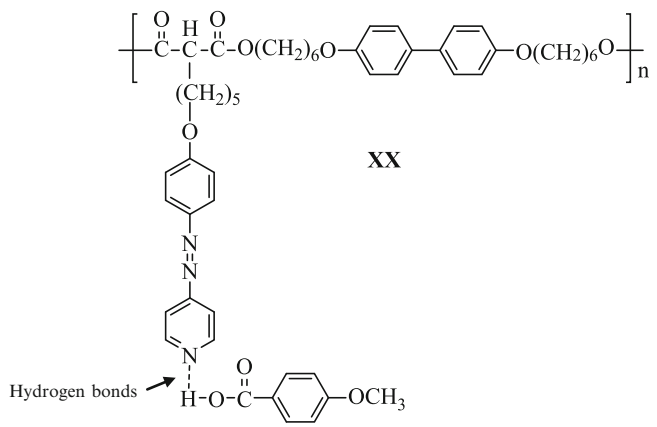
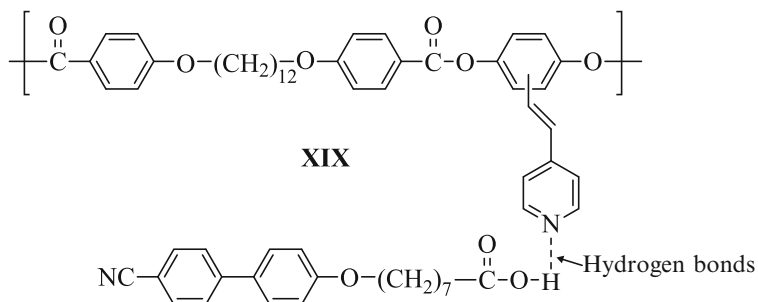
Note: *g* glass transition temperature, *k* melting temperature, *n* nematic phase, *i* isotropic state

are referred to as non-covalent interactions like hydrogen bonding, ionic interactions, electrostatic interactions, dipole-dipole interactions, π - π interactions, and metal-ion coordination, and the strength of these interactions ranges from 20 to 250 kJ/mol (Lehn 1988). Liquid crystalline anisotropies are a consequence of inter- and intramolecular-specific electronic and steric interactions. These interactions lead to the liquid crystalline long range order, which distinguishes mesophases from ordinary isotropic state (Kato and Mizoshita 2002). On one hand, the increased aspect ratio of supramolecular structure relative to constituent molecules stabilizes the mesophase of self-assembled systems. On the other hand, the anisotropy in the liquid crystal strongly enhances the strength of specific interactions (e.g. hydrogen bonding). Therefore, there is a strong cooperativity between association and induction of the liquid crystalline phase.

Huang and Han (2006) developed self-assembly strategy for building up the architecture of MCSCLCPs by specific interactions. In the first place, two different methods were used to obtain self-assembled MCSCLCPs by hydrogen bonding. The first method was to synthesize a main-chain liquid crystalline polymer with pendent pyridyl groups and then to combine, via hydrogen bonding, with a small mesogenic molecule having carboxylic acid group in a solvent, giving rise to a self-assembled MCSCLCP (**XIX**). In other words, the formation of MCSCLCP (**XIX**) was realized by hydrogen bonding between two mesogenic compounds. MCSCLCP (**XIX**) had a significant degree of hydrogen bonding at temperatures even above its clearing temperature as determined by temperature-dependent FTIR spectroscopy and underwent a glass transition at ca. 54 °C and a nematic-to-isotropic transition at ca. 154 °C. The second method employed was to first synthesize a main-chain liquid crystalline polymer having nonmesogenic side chain with azopyridyl group and then to combine, via hydrogen bonding, with a small nonmesogenic molecule (*p*-anisic acid) having carboxylic acid group in a solvent, giving rise to a self-assembled MCSCLCP (**XX**). In other words, the formation of MCSCLCP (**XX**) was realized by hydrogen bonding between the nonmesogenic azopyridyl group in the side chain of a MCLCP and a small nonmesogenic molecule having carboxylic acid group. MCSCLCP (**XX**) had a moderate degree of hydrogen bonding at temperatures even above its clearing temperature as determined by in situ FTIR spectroscopy and had a melting temperature of ca. 120 °C and a smectic-to-isotropic transition temperature of ca. 161 °C. The role of hydrogen bonding in the formation of self-assembled MCSCLCPs was investigated using in situ Fourier Transform Infrared (FTIR) spectroscopy.

Ionic interactions belong to the catalog of specific interactions that have higher strength than hydrogen bonding. A self-assembled MCSCLCP (**XXI**) was synthesized via ionic interactions between the nonmesogenic azopyridyl group in the side chain of an MCLCP and the sulfonic acid group in a small nonmesogenic molecule (*p*-toluenesulfonic acid) (Huang and Han 2006). MCSCLCP (**XXI**) had a glass transition temperature of ca. 58 °C, a melting temperature of ca. 110 °C, and a smectic-to-isotropic transition temperature of ca. 155 °C. Also, it showed strong ionic interactions persisting at temperatures well above the clearing temperature, as

determined by in situ FTIR spectroscopy. This observation explained why mesophase structure reappeared very quickly upon cooling from the isotropic state.



12.3 Supramolecular Ordering and Properties of Combined Main-Chain/Side-Chain Liquid Crystalline Polymers

The liquid crystallinity and supramolecular ordering of MCSCLCPs have immense impact on their performance, and thus numerous endeavors have been paid to gain in-depth insights into phase structures of these polymers. From the perspective of chemistry, a lot of strategies can be developed to tailor liquid crystalline properties of MCSCLCPs through the selection of mesogenic groups for both main-chain and side-chain of the polymer, altering the location of mesogens, and varying the length and types of flexible spacers. Indeed, the interplay between main chain and side chain of MCSCLCPs gives rise to the flexibility and versatility of liquid crystalline properties and supramolecular structures of these polymers. As aforementioned, a variety of MCSCLCPs have been accomplished in the past three decades, and accordingly, the correlation between liquid crystalline behavior and supramolecular structures have been elaborated on.

The thermal transition temperatures are generally measured by differential scanning calorimetry, and it has been demonstrated that the mesophase temperature range is surprisingly broadened in MCSCLCPs in comparison to the corresponding main-chain or side-chain LCPs. This can be ascribed to a synergistic stabilization of the mesophase between main-chain and side-chain mesogenic units in MCSCLCPs. Based on thermodynamic theory, Endres et al. (1990) investigated the structure-property relationship of MCSCLCPs. It was found that thermodynamic properties were governed by both enthalpy and entropy contributions from main-chain and side-chain mesogens in MCSCLCPs. Not only was the transition entropy strongly decreased with a decrease in spacer length, but also the transition enthalpy was a function of the length of flexible spacer. Thus, the side-chain arrangement and their interactions among themselves and with main-chain mesogens were crucial in controlling phase transition temperatures.

Polarized optical microscope has been widely used for detecting textures of mesophases of MCSCLCPs. In most cases, thin films are prepared by solution casting and placed between two glass slides. The temperature is controlled by a hot stage and real-time images can be taken for recording the variation of mesophase during heating and/or cooling cycles. Each type of mesophase has its characteristic pattern due to the macroscopic orientational order present in the sample. Furthermore, light scattering methods can be also employed for studying orientation correlations on a macroscopic scale for mesophases of MCSCLCPs. Moreover, electron microscopy was also employed to analyze structures of MCSCLCPs. Based on the observation of dark-field electron microscopy and electron diffraction, Voigt-Martin et al. (1988) concluded that the smectic layer spacing in MCSCLCPs, which did not correspond to spacings of the pure main-chain system, indicated that while molecular chains were fully extended in the oriented crystalline main-chain system, they were also forced to bend in MCSCLCPs. Nematic phases could occur only in those cases where there was a large difference between the length of the

main-chain and side-chain spacers. Combined MCSCLCPs with mesogenic side-chain groups grafted onto the main-chain mesogen units normally exhibited exclusively nematic mesophases.

However, the orientational order of MCSCLCPs on a supramolecular scale has to be examined by powder wide angle X-ray diffraction (WAXD) techniques (Donald and Windle 1992). MCSCLCPs have rich mesophases including nematic, smectic A, smectic C and higher ordered smectics quite in analogy to low molecular-weight liquid crystals. For a nematic mesophase, there exhibits a weak diffuse inner ring in WAXD patterns, which is associated with the length of molecules, and a strong diffuse ring at larger angles, indicative of the distance between neighboring molecules. The cholesteric mesophase shows a diffraction pattern similar to nematic mesophase. The diffraction pattern of the cholesteric mesophase is very similar to that of the nematic mesophase, and the existence of cybotactic groups can be also identified. The WAXD pattern of smectic A mesophase is characterized by one or more sharp inner reflections, which is related to smectic layers, as well as one diffuse outer ring, which is attributed to the short range order within layers. The WAXD pattern of smectic C is very similar to that of smectic A mesophase, but long axes of molecules are tilted with respect to the layer normal. The X-ray diffraction patterns of melt-drawn fibers of MCSCLCPs also throw light on the orientation of side-chain mesogens with main-chain mesogens.

Effects of chemical structures of achiral main-chain and chiral side-chain mesogens on the smectic layer spacing and on the formation of the superstructure were investigated by Mensinger et al. using small-angle X-ray scattering (SAXS) technique (Mensingher et al. 1992). Novel supramolecular structures for these chiral MCSCLCPs were revealed, which corresponded to bilayered and trilayered structures in smectic phases. Antiferroelectric ordering and ferroelectric ordering were assigned for the bilayered and trilayered structures, respectively, based on temperature-dependent SAXS data and the structure-property relationships for low molecular weight liquid crystals with similar chemical structures. Small angle neutron scattering (SANS) was also used for understanding synergistic interactions between main-chain mesogens and side-chain mesogens (Noirez et al. 1995). SANS results indicated that main-chain mesogens oriented parallel to the director, and thus MCSCLCPs was an intermediate state between main-chain LCPs and side-chain LCPs.

Furthermore, dielectric spectroscopy has also been examined to understand the supramolecular structure of MCSCLCPs. By doing this, Kremer et al. (1989) observed three relaxational processes related to the position and movement of side-chain mesogens in MCSCLCPs. These included an α -relaxation due to the glass process of the polymeric main chain coupled with side chain movements through spacers, a β_S -relaxation arising from the rotation of the mesogenic side chain around its long axis, and a β_m -relaxation, which was assigned to the rotation of the mesogenic group in the main chain around its long axis. By using broad-band dielectric spectroscopy, Endres et al. (1987) discovered that the rotation of side-chain mesogens relative to main-chain mesogens was not as strongly restricted as in side-chain liquid crystalline polymers. Thus, they attributed this to the fact that

side-chain mesogens were attached onto the flexible spacer within the main-chain backbone and that the concentration of side chains was comparatively small.

Yang et al. (2012) utilized semi-flexible chain self-consistent field theory (SCFT) coupled with the pseudospectral method to study isotropic-anisotropic phase transitions and conformation variations for MCSCLCPs. They considered two major interactions in their model, that is, the global coupling between backbone segments, between main-chain and side-chain mesogens, and between side-chain mesogens themselves, as well as the local coupling between main-chain mesogens and side-chain mesogens. The simulation results showed that when hinges were flexible, both global and local effects preferred parallel alignments of main-chain and side-chain mesogens, forming prolate uniaxial nematic phase. If the hinges were relatively stiff, the competition between global interaction preferring parallel orientations of the system and the perpendicular tendency of two components due to the comb architecture resulted in rich phases with various orientation modes.

12.4 Conclusions and Outlook

The combined main-chain/side-chain liquid crystalline polymers (MCSCLCPs) possess a unique hybrid structures, which combine chemical features of both main-chain and side-chain liquid crystalline polymers (LCPs). Because of the synergistic effect, the temperature range of thermal transition of mesophases for MCSCLCPs is largely broadened relative to the corresponding main-chain or side-chain LCPs. Such a synergistic effect may also lead to the breakthrough in properties of LCPs. For instance, the combination of high-modulus main-chain LCPs with flexible side-chain mesogens may afford excellent melt processability while maintaining high modulus and strength of main-chain LCPs. On the other hand, MCSCLCPs open new pathways to introduce a variety of functional groups into main-chain and/or side-chain mesogens, and thus lead to the formulation of advanced materials with tailored properties and desired supramolecular structures.

Judicious molecular design is required for achieving MCSCLCPs with biaxial orientation, which may endow resultant products with uniform bulk properties. This may overcome the deficiency of uniaxial orientation of conventional LCPs during processing, which results in good properties in one direction but poor properties in the other direction. Although sophisticated design principles are still not available, basic rules of thumb include dissimilar mesogens for pushing away side-chain mesogens from main-chain mesogens and controllable flexible spacers. Therefore, it is of utmost importance to gain better understanding of interactions between main-chain and side-chain mesogens. Among others, the rigidity of main-chain backbone, density of main-chain and side-chain mesogens and stereoregularity also play a crucial role in regulating the orientation of side-chain mesogens. Owing to their outstanding properties with proper structural designs, MCSCLCPs can be applied in many areas such as engineering plastics and optical and electro-optical devices.

The other possibility is to incorporate side-chain mesogens with high dipole-moment such that the main-chain mesogen would align along with the polymer flow while a magnetic field may be applied to induce the side-chain mesogens to orient perpendicular to the main-chain backbone. Due to the advancement of synthetic technology (e.g. living or controlled polymerization), MCSCCLCPs can be integrated into other polymers, thus forming block copolymers. This will lead to hierarchical structures with various topologies and open new opportunities for exploiting new functional materials with fine-tuning ordered structures. The attachment of side-chain mesogens onto a rigid-rod backbone, especially for biomacromolecules, broadens the scope of MCSCCLCPs and enables the synthesis of high-performance materials from renewable sources. The MCSCCLCPs can be further exploited for creating networks by crosslinking reactions (Zentel and Reckert 1986; Zentel et al. 1989; Pakula and Zentel 1991), thus forming combined main-chain/side-chain liquid crystalline elastomers for unusual mechanical properties.

Self-assembly by specific interactions offers an easier and more efficient methodology to create a new spectrum of MCSCCLCPs. Self-assembly driven by hydrogen bonding and ionic interactions have been extensively investigated, and other specific interactions like metal ion interactions and Coulombic interactions will be of particular interests to explore. The supramolecular structures observed in self-assembled MCSCCLCPs have thrown new light on the effect of side-chain mesogens induced by specific interactions on structure-property relationships. Future endeavor may direct toward the introduction of chiral nematic or ferroelectric systems via self-assembly for various opto-electronic and nanotechnology applications.

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