Mesogen-Jacketed Liquid Crystalline Polymers: Molecular Design and Synthesis

2

Zhihao Shen

Contents

Definition 30
Introduction 31
LC Phases of MJLCPs 32
Special Properties of MJLCPs 35
Molecular Design 38
Chemical Structure-Phase Behavior Relationships 39
Molecular Design for MJLCPs 41
Synthesis 42
Conventional Free Radical Polymerization 42
Controlled Radical Polymerization 44
Atom Transfer Radical Polymerization (ATRP) 45
Ring-Opening Metathesis Polymerization (ROMP) 50
Transition Metal-Catalyzed Metathesis Polymerization 50
Polymer Reaction 51
Supramolecular Approaches 53
Future Directions 54
References 55

Abstract

Mesogen-jacketed liquid crystalline polymers (MJLCPs) are rigid side-chain polymers that can form columnar and smectic liquid crystalline (LC) phases. Their liquid crystallinity is dependent on the molecular weights (MWs), and many MJLCPs exhibit reentrant phase behaviors. The size of the structure formed by an MJLCP,

Z. Shen (✉)
Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing, China
e-mail: zshen@pku.edu.cn

© Springer Nature Switzerland AG 2020

L. Zhu, C. Y. Li (eds.), *Liquid Crystalline Polymers*, Polymers and Polymeric Composites: A Reference Series, https://doi.org/10.1007/978-3-030-43350-5_48

either columnar or smectic, is directly correlated with the size of the side chain. While the first MJLCPs have laterally attached mesogenic side chains, bulky side chains that are not mesogenic can also be used to construct MJLCPs. The "jacketing" effect, i.e., the steric hindrance caused by the densely packed side chains, forces the polymer backbone to take an extended-chain conformation. Many factors, such as MW, backbone flexibility, tail length, and architecture, influence the phase behaviors of MJLCPs. With the understanding of the chemical structure-phase behavior relationships, molecular design for MJLCPs can be executed by carefully choosing molecular parameters including the shape and rigidity of the side chain, the structure of the polymer backbone, and so on. MJLCPs can be synthesized by radical polymerizations that do not require highly pure solvents and reagents. Many controlled/living radical polymerization methods, such as nitroxide-mediated radical polymerization (NMRP) and atom transfer radical polymerization (ATRP), can also be employed. Recently, another living polymerization method, ring-opening metathesis polymerization (ROMP), has been applied in the synthesis of MJLCPs with a polynorbornene backbone. With the use of such controlled polymerization methods, the length of the rodlike or sheetlike MJLCP chain can be tuned by adjusting the MW. In addition, MJLCPs can also be synthesized by polymer reactions from prepolymers like poly(methylsiloxane)s. Furthermore, MJLCPs can also be obtained by taking advantage of supramolecular chemistry, with the application of hydrogen bonding, ionic interaction, and other non-covalent interactions. Future directions in the study of MJLCPs will be to address the main challenges by designing monomers that can be more easily synthesized and polymerized, establishing cost- and time-saving synthetic methods, applying calculation and computer simulation that can accurately predict phase behaviors and guide molecular design, and developing functional MJLCP materials.

Keywords

Mesogen-jacketed liquid crystalline polymer · "Jacketing" effect · Liquid crystalline phase · Columnar phase · Smectic phase · Structure-property relationship · Free radical polymerization · Controlled/living radical polymerization · Nitroxide-mediated radical polymerization (NMRP) · Atom transfer radical polymerization (ATRP) · Reversible addition-fragmentation chain transfer (RAFT) · Ring-opening metathesis polymerization (ROMP)

Definition

Mesogen-jacketed liquid crystalline polymers (MJLCPs) are side-chain polymers that have significant chain rigidity and form liquid crystalline (LC) phases. The first MJLCPs have laterally attached mesogenic side chains that are connected to the polymer backbone via a short spacer or with one carbon-carbon single bond. With further understanding of these LC polymers (LCPs), side chains of MJLCPs can also be bulky ones that are not mesogenic.

Introduction

Generally, a liquid crystalline polymer (LCP) is categorized as main-chain liquid crystalline polymer (MCLCP), side-chain liquid crystalline polymer (SCLCP), or main-chain/side-chain liquid crystalline polymer (MCSCLCP) combined one if the mesogenic unit is incorporated into the backbone, the side chain, or both of the polymer, respectively (Wang and Zhou 2004). For SCLCPs and MCLCPs, the mesogen can be introduced into the polymer either longitudinally (end-on) or laterally (side-on) (McArdle 1989), as shown in Fig. 1.

Mesogen-jacketed liquid crystalline polymers (MJLCPs), sometimes also known as rigid side-group-type liquid crystalline polymers (LCPs), were first proposed and synthesized by Zhou et al. in the late 1980s (Zhou et al. 1987, 1989). Historically, this can be regarded as the third way for synthesizing LCPs, in addition to the synthesis of MCLCPs and traditional SCLCPs. On the one hand, chemically speaking, the first MJLCPs are like side-on SCLCPs with side-chain mesogens laterally attached to the polymer backbone. From the molecular design perspective, the lateral attachment of the mesogen was adopted under the consideration that the influence of the supposedly random-coiled main chain could be alleviated when the connection was at the gravity center of the mesogen. However, unlike conventional side-on SCLCPs containing relatively long flexible spacers which are used to decouple the dynamics of the backbone and the side-chain mesogens on the basis of the decoupling concept proposed by Finkelmann and coworkers (Finkelmann et al. 1978; Hessel and Finkelmann 1985, 1986), MJLCPs have very short spacers or without any spacers at all. On the other hand, because of the closer attachment of the mesogenic side groups to the polymer backbone, there is a strong steric effect (or "jacketing" effect, which is also important in forming LC structures of dendron-jacketed polymers proposed by Percec and coworkers (Percec and Tomazos 1992; Rosen et al. 2009; Rudick and Percec 2008) owing to the densely packed, bulky side groups. As a result, the polymer backbone is forced to take an extended-chain conformation, leading to a rigid or semirigid chain (Chen et al. 2010). Therefore, MJLCPs possess physical properties similar to those of MCLCPs. In addition, the whole MJLCP polymer chain can serve as a supramolecular mesogen to form liquid crystalline (LC) phases. Depending on the side chain, the MJLCP supramolecular mesogen can be rodlike or sheetlike, resulting in columnar or smectic LC phases, respectively (Fig. 2). Mesogenic side chains were used in the first MJLCPs (polymers **1** and **2** in Chart 1). MJLCPs containing non-mesogenic side groups can also be liquid crystalline if the side chains can induce a strong enough

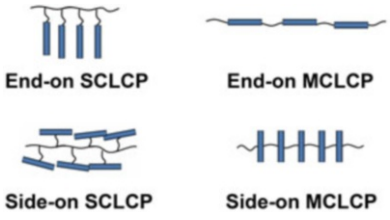


Fig. 1 Schematic illustration of structural models of LCPs. (Reprinted and adapted with permission of the Royal Society of Chemistry Chen et al. 2010)

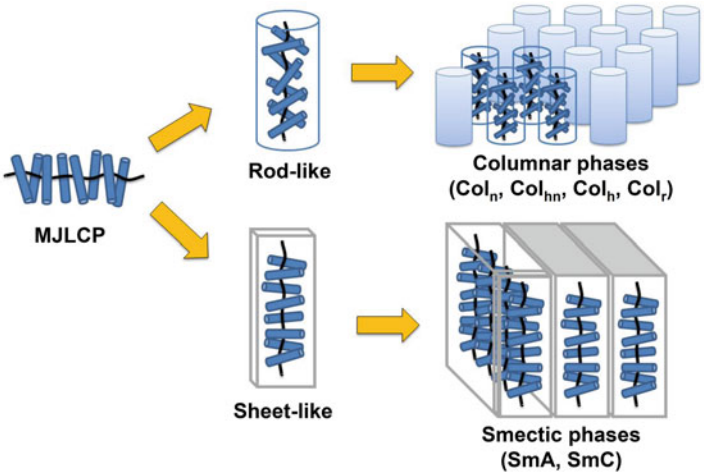


Fig. 2 Schematic representation of different LC phases formed by MJLCPs. (Reprinted and adapted with permission of the Royal Society of Chemistry Chen et al. 2010)

"jacketing" effect, and even polymer **3** in Chart 1 is liquid crystalline when the length of the alkoxy tails is appropriate.

The sizes of the LC structures formed by MJLCPs are closely correlated with the side chains. For a rodlike MJLCP, the diameter of the supramolecular rod is determined by the size of the side chain, while the length increases linearly with increasing degree of polymerization (DP) which can be controlled when controlled/living polymerization methods are used. Such a rodlike chain with tunable dimensions can serve as an excellent building block in constructing novel LC block copolymers.

LC Phases of MJLCPs

As supramolecular mesogens, rodlike MJLCPs can form various columnar phases with the parallel alignment of the polymer chains. On the other hand, sheetlike MJLCPs containing side chains with more rigidity or special interactions can self-organize into smectic phases, and the polymer main chains are embedded in the smectic layers and possess a parallel alignment.

Columnar Phases of MJLCPs

Nematic phases of the first MJLCPs (polymers **1** and **2** in Chart 1) synthesized were initially proposed on the basis of polarized light microscopy (PLM) results (Zhou et al. 1987, 1989). In fact, such nematic phases are columnar nematic (Col_n) phases developed by the rodlike MJLCP supramolecular mesogen, with the consideration of the jacketed model. Many other MJLCPs also exhibit Col_n phases (Jin et al. 2010;

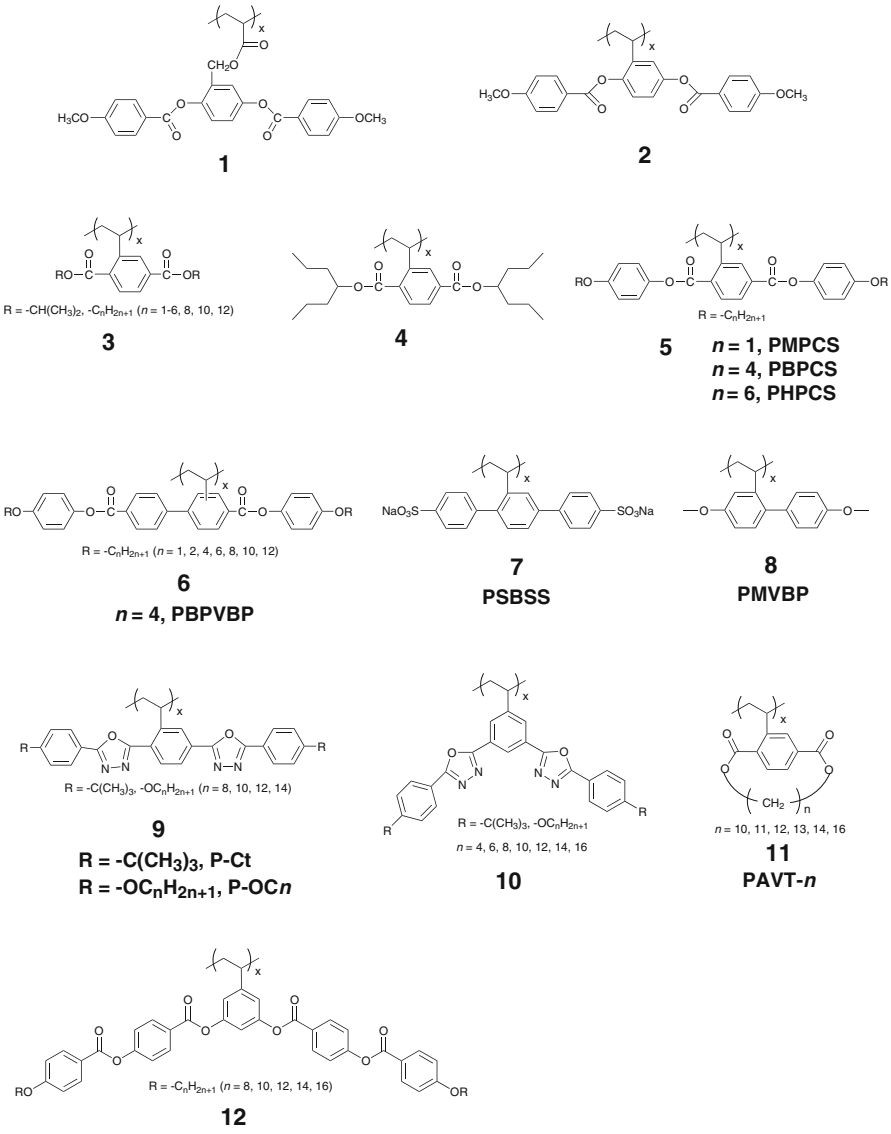


Chart 1 Structures of some MJLCPs

Ye et al. 2004). Some MJLCPs form more ordered columnar phases such as two-dimensional (2D) hexagonal columnar (Col_h) (Chen et al. 2006b; Tu et al. 2000; Xu et al. 2009) and rectangular columnar (Col_r) (Chen et al. 2006b) phases. Polymer **4** (Chart 1) with a non-mesogenic bulky side group was first determined by wide-angle X-ray diffraction (WAXD) to exhibit a Col_h structure (Tu et al. 2000).

In the 2D WAXD fiber pattern of polymer **4** (Fig. 3), there are three low-angle diffractions on the equator. The diffractions have a scattering vector ratio of $1:3^{1/2}:4^{1/2}$, indicating a 2D hexagonal packing. The three diffractions can be assigned as 100, 110, and 200 diffractions of the Col_h phase.

PMPCS (polymer **5** with $n = 1$ in Chart 1) is a frequently used MJLCP. Figure 4 shows the 2D WAXD pattern of a fiber sample of PMPCS with a relatively high MW (Ye et al. 2004). The X-ray beam was parallel to the fiber direction. The result indicates a local sixfold symmetry of the lateral packing of the PMPCS rods. Because no higher-order diffractions are observed, the order of the LC phase is not long-range and is between those of the Col_n and Col_h phases. The LC phase is assigned as hexatic columnar nematic (Col_{hn}).

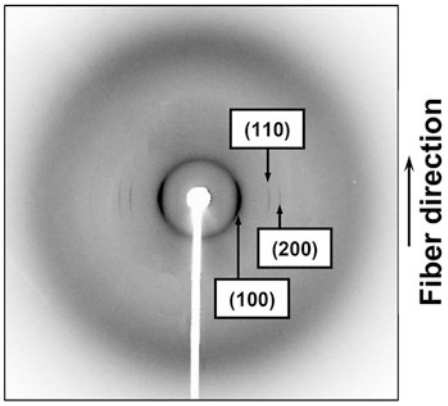


Fig. 3 2D WAXD pattern of an oriented fiber of polymer **4**. (Reprinted with permission of the American Chemical Society (Tu et al. 2000) and Royal Society of Chemistry (Chen et al. 2010))

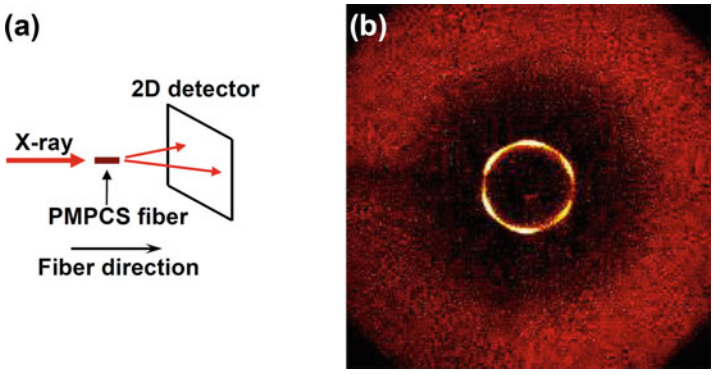


Fig. 4 Geometry of experimental setup in the 2D WAXD experiment with the X-ray incident beam parallel to the fiber axis (**a**) and 2D WAXD fiber pattern of the sample (**b**). (Reprinted with permission of the American Chemical Society (Ye et al. 2004) and the Royal Society of Chemistry (Chen et al. 2010))

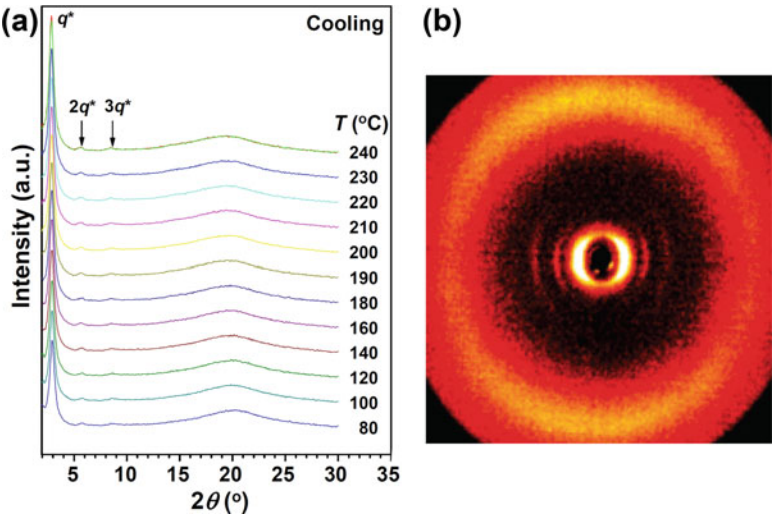


Fig. 5 1D (**a**) and 2D (**b**) WAXD patterns of polymer **6** PBPVBP. (Reprinted and adapted with permission of the American Chemical Society Chen et al. 2007)

Smectic Phases of MJLCPs

The MJLCP with semifluorinated tails in the side group synthesized by Ober et al. exhibits a smectic C (SmC) phase (Gopalan et al. 2002). The microphase separation between fluorinated components and hydrocarbons plays an important role in the formation of the smectic phase.

When more rigid side-chain cores, which usually lead to increased side-chain rigidity and interactions, are introduced into MJLCPs, smectic phases can develop. PBPVBP (polymers **6** with $n = 4$ in Chart 1) shows a smectic A (SmA) phase (Chen et al. 2007). As shown in Fig. 5a, the 1D WAXD profiles of the polymer display three strong low-angle diffraction peaks with a scattering vector ratio of 1:2:3, indicating a smectic structure. The SmA phase is identified from the 2D WAXD pattern (Fig. 5b), in which the strong diffractions attributed to the layered structures and the amorphous scattering owing to the lateral packing of the MJLCP supramolecular mesogens are perpendicular to each other. Polymer **6** with longer alkoxy tails forms SmC phases (Chen et al. 2009).

Special Properties of MJLCPs

Chain Rigidity

The rigidity of MJLCPs was proposed when the first MJLCPs were reported (Zhou et al. 1987, 1989), after which Hardouin et al. performed small-angle neutron scattering (SANS) studies on side-on SCLCPs (Hardouin et al. 1991, 1992). Their results confirmed the rigidity of the polymers and the jacketed model.

The MJLCPs synthesized by Zhou et al. (1989) exhibit banded textures (Xu et al. 1993a, b) under PLM usually observed in oriented rigid or semirigid polymers such as MCLCPs (Wang and Zhou 2004), confirming that these polymers have significant chain rigidity. Actually, these polymers are the first side-chain polymers that show banded textures. Many other MJLCPs also display similar banded textures (Tu et al. 2000; Ye et al. 2004; Zhou et al. 1993).

The chain stiffness of polymer **2** (Chart 1) was studied with static light scattering and viscometry (Wan et al. 1995). The persistence length was estimated to be about 12 nm, and the α-value in the Mark-Houwink-Sakurada equation was determined to be 0.82. These results indicate that the polymer has a wormlike chain conformation in dilute solution, similar to MCLCPs.

Small-angle X-ray scattering (SAXS) was used to study the conformation of a mesogen-jacketed polyelectrolyte, poly[sodium 2,5-bis(4′-sulfophenyl)styrene] (PSBSS, polymer **7** in Chart 1) in aqueous solution (Qu et al. 2014). The precursor of PSBSS was synthesized by atom transfer radical polymerization (ATRP), resulting in a narrow MW distribution (MWD). PSBSS in the aqueous solution has a cylindrical conformation, with a persistence length of 11.5 nm.

MW Dependence

For a rodlike MJLCP with a stretched backbone, its length increases almost linearly with increasing molecular weight (MW) and thus affects the aspect ratio of the rodlike supramolecular mesogen. Therefore, the LC behavior of the MJLCP has a strong MW dependence (Chen et al. 2010). The typical MJLCP PMPCS shows such an MW-dependent phase behavior (Ye et al. 2004). When its MW measured by GPC is lower than 1.0×10^4 Da, PMPCS is amorphous; when the MW is in the range of 1.0×10^4–1.6×10^4 Da, it forms a stable $\mathrm{Col_n}$ LC phase upon heating at high temperatures above its glass transition temperature (T_g); when the MW is higher than 1.6×10^4 Da, it is also liquid crystalline after being annealed at temperatures higher than T_g, exhibiting a $\mathrm{Col_{hn}}$ phase. Many other MJLCPs, such as PBPCS (polymer **5** with $n = 4$ in Chart 1) (Zhao et al. 2006) and PMVBP (polymer **8** in Chart 1) (Zhang et al. 2014), also exhibit similar MW-dependent phase behaviors.

Unusual Phase Behavior

Many as-prepared MJLCP samples are amorphous and enter into LC phases when they are heated or annealed at temperatures higher than their T_g values. If the isotropization temperatures of the LC phases are too high to be observed under experimental conditions, the LC phases will be retained during further heating or subsequent cooling processes. However, unusual phase behaviors have been observed in some MJLCPs (Chen et al. 2010), similar to the reentrant phase behaviors owing to the rod-coil conformational transformation in polypeptides (Lin 1997) and the columnar-isotropic transition in polydialkoxyphosphazenes (Papkov et al. 1992). Such a behavior was first found in PHPCS (polymer **5** with $n = 6$ in Chart 1) (Yu et al. 2003a), which became isotropic liquid again after being

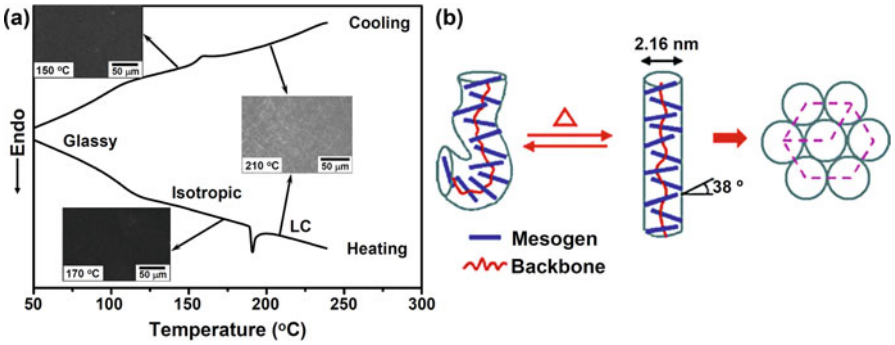


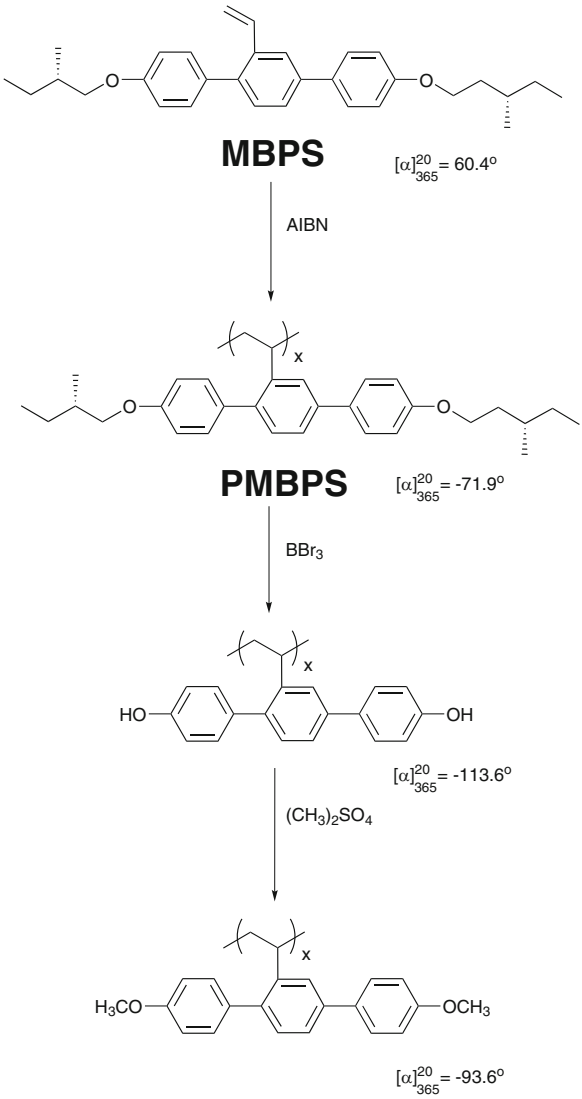
Fig. 6 Unusual phase behavior of PBPCS (polymer **5** with $n = 4$). (**a**) DSC thermograms show enantiotropic transitions which have small but non-negligible latent heat. PLM results (inset micrographs) show that the sample is birefringent at high temperatures, indicating the existence of a mesophase, while the sample is isotropic at low temperatures. (**b**) The wormlike chain changes to a rodlike chain during heating, which is driven by entropy, and this transformation is reversible upon cooling. The rods self-organized into a Col_{hn} phase which has weak lateral hexagonal order. (Reprinted and adapted with permission of the American Chemical Society (Zhao et al. 2006) and the Royal Society of Chemistry (Chen et al. 2010))

cooled from the LC phase. The similar behavior in PBPCS was confirmed by experimental results such as those of differential scanning calorimetry (DSC) and PLM, as shown in Fig. 6 (Chen et al. 2010; Zhao et al. 2006). The unusual transition from the isotropic liquid to the LC phase during heating is entropy driven, which can be rationalized by the higher entropy gain owing to the increased freedom of side chains when the MJLCP is in the LC state compared to the entropy loss of the main chain in the ordered LC phase.

Chirality Transfer

MJLCPs have interesting behaviors in chirality transfer. As shown in Scheme 1, the MJLCP PMBPS with chiral groups attached at the ends of the side-chain mesogen has a helical secondary structure formed during the free radical polymerization (Yu et al. 2003b). The helical conformation is maintained even when the chiral groups are chemically removed from the side chain.

During the free radical polymerization of bulky vinyl monomers containing laterally attached p-terphenyl groups and a single asymmetric center, the stereogenic centers in the side chains of the monomers can transfer the chirality to the propagating polymer chains (Cui et al. 2009). In addition, optically active helical mesogen-jacketed copolymers obtained from the radical copolymerization of a chiral monomer and an achiral monomer display an unusual linear optical activity-composition relationship, in sharp contrast to the "sergeants-and-soldiers" and "majority" rules (Cui et al. 2010).



Scheme 1 Synthesis of chiral MJLCPs and their chiroptical properties (Yu et al. 2003b)

Molecular Design

Because many factors, including MW (which has been described in the previous section), backbone flexibility, tail length, architecture, and so on, strongly affect the phase behaviors of MJLCPs (Chen et al. 2010), it is necessary to understand the relationships between the chemical structure and the phase behavior. Then, a rational

molecular design can be preceded. It should be noted that owing to the complex chemical structures of MJLCPs, some of the abovementioned factors may be intertwined and may not be separated.

Chemical Structure-Phase Behavior Relationships

Backbone Flexibility

Most MJLCPs are based on polyacrylates/polymethacrylates and polystyrenes, and they all have a polyethylene backbone. When the backbone is changed to more flexible polysiloxane, the phase structures of MJLCPs are not exactly the same (Zhang et al. 2010). MJLCPs with the more rigid polyacetylene backbone tend to form smectic phases compared to their polystyrene analogs (Chen et al. 2006a). Although polynorbornene appears to be a more rigid main chain than polyethylene, the length of the repeating unit of polyethylene is only half those of polynorbornene, and the side-chain density in the polynorbornene-based MJLCP is only half that in the polyethylene-based MJLCP. Therefore, the overall rigidity and the LC-forming ability of a polynorbornene-based MJLCP are determined by the side chain attached. In the MJLCPs synthesized with a polynorbornene backbone, polymers with side chains having longer alkyl tails are liquid crystalline (Zhu et al. 2014b). In addition, they have lower isotropization temperatures and become isotropic upon heating.

Molecular Shape of Side Chain

Following the change of the linear rigid side-chain core in polymer **9** to a bent-type core, all the resultant polymers **10** form Col_h instead of SmA phases (Chai et al. 2007; Xu et al. 2009). And MJLCPs having dendrons in the side chains also show columnar phases (Jin et al. 2010). Similarly, with the introduction of a triphenylene (Tp) moiety in the side chain, the shape of a polyacetylene-based MJLCP changes to columnar and exhibits a Col_h phase instead of smectic phases for many MJLCPs with a polyacetylene backbone (Yu et al. 2013).

Rigidity of Side Chain

Polymer **11** in Chart 1 having cyclic side groups of appropriate sizes is liquid crystalline (Mei et al. 2010, 2012). The liquid crystallinity is attributed to the rigidity of the cyclic pendants and the whole polymer chain.

Aliphatic Tail of Side Chain

The effect of alkyl tails on the phase behaviors of MJLCPs is frequently observed. For example, the phase structure of polymer **3** in Chart 1 shows a strong dependence on the length of side-chain aliphatic tails (Fig. 7) (Yin et al. 2003). Polymers with side chains having propyl/isopropyl to hexyl tails form highly ordered 2D Col_h phases. Polymers having tails of other lengths are either partially liquid crystalline or even amorphous.

When the length of aliphatic tails is increased, the LC phase of the MJLCP **6** (polymerized from 2-vinyl monomers) in Chart 1 changes from SmA ($n = 2, 4$) to SmC

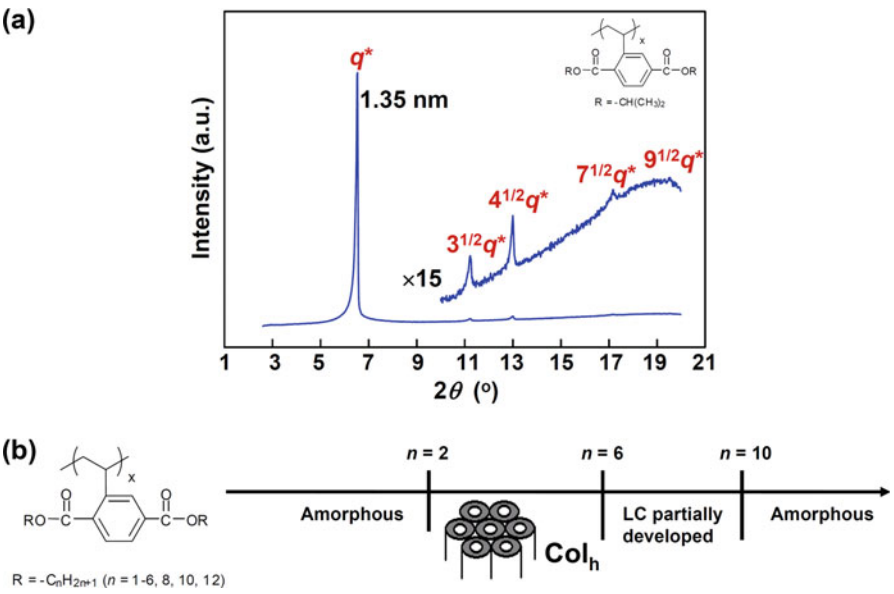


Fig. 7 Tail length dependence of the phase structure for polymer **3**. (**a**) 1D WAXD pattern of polymer **3** (R = $-CH(CH_3)_2$) indicates a highly ordered 2D Col_h phase of the sample. (**b**) Phase structure of polymer **3** depends on the structure or length of the flexible tails in the side groups. The long-range 2D Col_h phase is only formed when side chain contains propyl/isopropyl to hexyl tails. The polymer is less ordered for other tails. (Reprinted and adapted with permission of the American Chemical Society (Yin et al. 2003) and the Royal Society of Chemistry (Chen et al. 2010))

($n = 6$, 8, 10, 12) (Chen et al. 2009). And polymer **9** (Chart 1) having 1,3,4-oxadiazole units in the side chains forms a Col_{hn} phase for P-Ct and changes to a SmA phase for P-OC*n* (Chai et al. 2007), confirming that the microphase separation between the flexible tails and the rigid core is also important in the formation of smectic structures. In addition, polymer **12** in Chart 1 with relatively short aliphatic tails forms a Col_r phase, while that with relatively long tails exhibits a Col_h phase. And both Col_h and Col_r phases are observed for polymer **12** with $n = 12$.

Non-covalent Interactions in Side Chain

Generally, the introduction of non-covalent interactions, such as hydrogen bonding, π-π stacking, ionic interaction, and microphase separation, into the side chains of MJLCPs favors the formation of smectic phases. For example, MJLCPs having side-chain amide linkages can develop SmA phases (Cheng et al. 2011a). Additionally, smectic phases in these polymers are also favored because of the increased immiscibility between the longer tails and the aromatic core. Similar phenomena have been observed in the two new series of polynorbornene-based MJLCPs (Yang et al. 2013; Zhu et al. 2014b). Only polymers with long enough alkoxy tails in the side group are liquid crystalline. MJLCPs having ionic groups in the side chains also display smectic phases (Cheng et al. 2011b).

Molecular Architecture

In the LC phases of MJLCPs, the MJLCP supramolecular mesogens are aligned parallel to one another. If the change in molecular architecture influences such a parallel alignment, the phase behavior will undoubtedly be affected.

The effect of architecture was elucidated in an eight-arm star PMPCS polymer which was synthesized by ATRP using an octafunctionalized initiator (Pan et al. 2007). The MW of each arm for the formation of the LC phase is lower than that of the linear PMPCS. In addition, the star polymer only exhibits the more ordered Col_{hn} phase. The result suggests that this molecular architecture favors the parallel packing of PMPCS chains. On the other hand, the hyperbranched structure is unfavorable for the formation of the more ordered LC phase, as a hyperbranded PMPCS copolymer synthesized by ATRP only shows a less ordered Col_n phase (Mei et al. 2008).

Molecular Design for MJLCPs

While the design of monomers for easier synthesis is also important, such molecular details will not be discussed. As abovementioned, many factors affect the phase behaviors of MJLCPs. Therefore, the molecular design for MJLCPs involves considerations on the detailed chemical structures of the backbones and side chains of the polymers. Molecular parameters, such as the shape and rigidity of the side chain, the structure of the polymer backbone, and so on, should be carefully selected on the basis of the chemical structure-phase behavior relationships of MJLCPs.

In addition, the size of the structure formed by an MJLCP, either columnar or smectic, is directly correlated with the size of the side chain. Therefore, the diameter of the supramolecular rod or the width of the sheetlike structure can be readily tuned by varying side chains (Chen et al. 2010).

The first MJLCPs based on polyacrylates have a short linkage between the side-chain mesogen and the main chain (Zhou et al. 1987). Later, polystyrene-based MJLCPs were synthesized, and the side-chain mesogen was attached to the backbone with just one carbon-carbon single bond (Zhou et al. 1989). Then, many series of polystyrene-based MJLCPs have been obtained, with flexible aliphatic tails at the ends of the mesogenic side chains. Most of the MJLCPs exhibit stable columnar phases. With the increase in the conjugation length or the rigidity of the side chain, polymers showing smectic LC phases are obtained.

In the molecular design of the first MJCLPs, mesogenic side chains were used. Different types of mesogens, including calamitic, bent-cored (Chen et al. 2006b; Xu et al. 2009), and discotic (Yu et al. 2013) ones, have been used in the side chains of MJLCPs. Because the liquid crystallinity of MJLCPs originates from supramolecular mesogens owing to the "jacketing" effect, it is not necessary to use mesogens in the side chain. Many series of MJLCPs with non-mesogenic side groups have been designed and synthesized (Tu et al. 2000; Zhang et al. 1999). Some of these MJLCPs exhibit isotropization temperatures before decomposition (Tu et al. 1999).

To obtain MJLCPs that form smectic phases, side chains with special interactions can be used. Microphase separation between incompatible segments in side chains favors smectic structures. And jacketed polymers containing side-chain functional groups with other non-covalent interactions like hydrogen bonding (Cheng et al. 2011a) and ionic interaction (Cheng et al. 2011b) can also show smectic phases.

In addition to polyacrylate/polymethacrylate and polystyrene main chains that are usually used, polysiloxane backbone has also been employed to prepare MJLCPs through hydrosilylation of polymethylhydrosiloxane with styrenic compounds (Zhang et al. 2010). Other than flexible main chains, more rigid backbones such as polynorbornene (Yang et al. 2013; Zhu et al. 2014b), polyacetylene (Chen et al. 2006a; Peng et al. 2010; Yu et al. 2013), and polythiophenes (Yang et al. 2009) have also been successfully introduced into MJLCP systems.

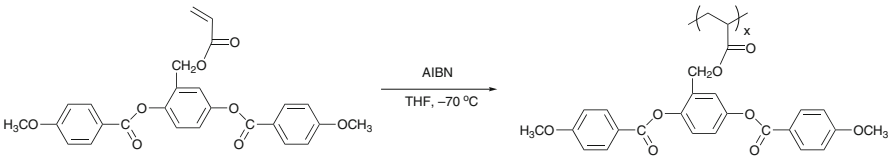
Synthesis

MJLCPs can be synthesized by radical polymerizations, including many controlled/living radical polymerization methods, which do not require highly pure solvents and reagents. Recently, another living polymerization method, ring-opening metathesis polymerization (ROMP), has been applied in the synthesis of MJLCPs with a polynorbornene backbone. ROMP was first used by Pugh et al. in the synthesis of polynorbornene-based side-on SCLCPs, resulting in polymers with controlled MWs and quite narrow MWDs (Pugh and Schrock 1992). MJLCPs can also be obtained by polymer reactions from prepolymers such as poly(methylsiloxane)s, similar to the case of the synthesis of some conventional SCLCPs. In addition, supramolecular approaches with non-covalent interactions such as hydrogen bonding and ionic interaction can be utilized to prepare MJLCPs.

Conventional Free Radical Polymerization

Because the monomers of many MJLCPs are vinyl ones, conventional free radical polymerization is frequently used. The first MJLCPs reported were obtained by this method (Zhou et al. 1987, 1989). One example is shown in Scheme 2. Similarly, many other series of MJLCPs have also been prepared via free radical polymerizations.

MJLCPs with quite bulky side groups can still be obtained. For example, polymers with dendrons (Chart 2) (Jin et al. 2010), Tp moieties (PP*n*V, Chart 3) (Zhu et al. 2012; Zhu et al. 2014a), and polyhedral oligomeric silsesquioxane (POSS) units (P*n*POSS, Chart 4) (Zhu et al. 2015) in the two ends of the side chains have been synthesized. The polymerization is more difficult compared to other monomers with less bulky side groups, which leads to limited DPs of the resulting polymers. For the MJLCPs with dendritic side groups, the second-generation polymer PCbzG2 has a lower DP than that of the first-generation one PCbzG1 even though the same conditions were used in the polymerization of the two polymers with different dendron generations. The conversion in the polymerization of the second-generation



Scheme 2 Synthesis of the first MJLCP by conventional free radical polymerization (Zhou et al. 1987)

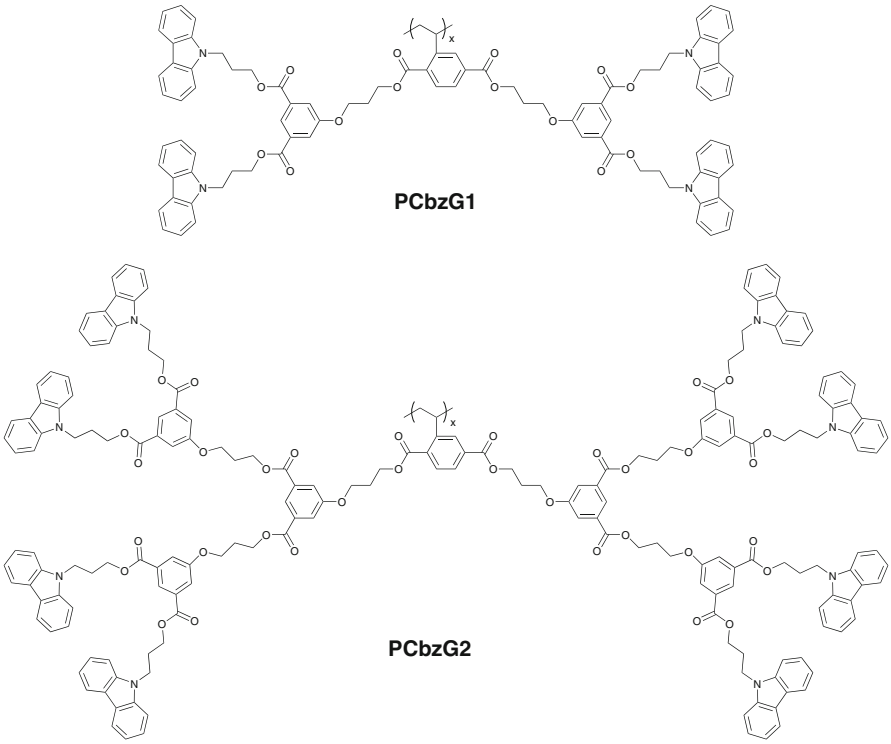


Chart 2 Chemical structures of the MJLCPs with dendrons in the side chains

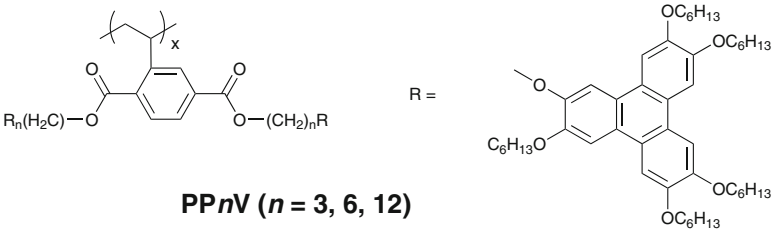


Chart 3 Chemical structure of PP*n*V

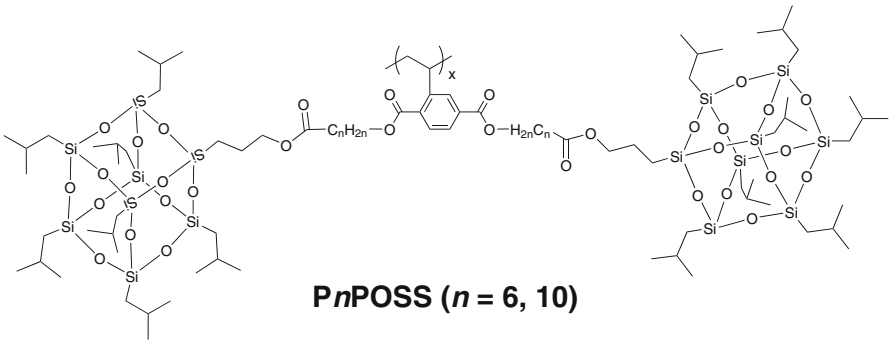


Chart 4 Chemical structure of P*n*POSS

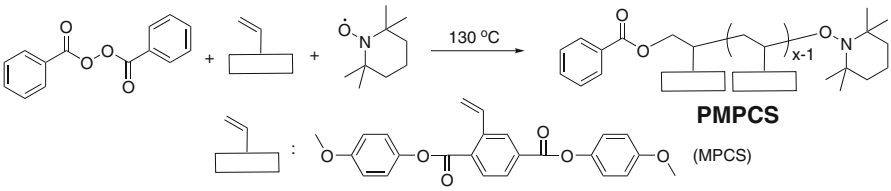
monomer was lower compared to that of the first-generation monomer, possibly owing to a lower concentration of the double bond and a stronger steric hindrance of the former. Nevertheless, these three types of polymers with quite bulky side groups all display LC behaviors. It should be noted that the polymers with Tp moieties are MCSCLCPs based on an MJLCP backbone because Tp is a typical discotic mesogen. The length of the spacer between the Tp units and the side-chain core plays an important role in regulating the competitive and synergetic interactions of the two different types of mesogens, the MJLCP backbone and the Tp discotic mesogen in the side chain, and determining the phase behavior of this PP*n*V MCSCLCP. For P*n*POSS, the phase behavior is also dependent on the length of the spacer between the crystalline POSS units and the side-chain core.

Controlled Radical Polymerization

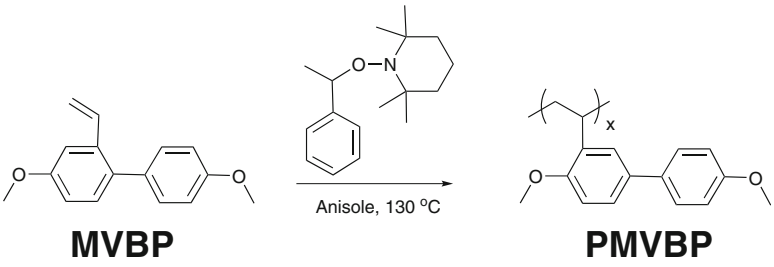
Although most MJLCPs can be easily polymerized from vinyl monomers using conventional free radical polymerizations, the resulting polymers usually have broad MWDs, which is not favorable for the study of relationships between LC phase behaviors and chemical structures. Owing to the presence of functional groups in the side chains of most MJLCPs, commonly used controlled/living polymerization methods such as anionic polymerization cannot be employed. However, the rapid development in controlled radical polymerizations, such as nitroxide-mediated radical polymerization (NMRP) and ATRP, makes it possible to synthesize MJLCPs with controlled MWs and MWDs (Chen et al. 2010; Gao et al. 2009).

Nitroxide-Mediated Radical Polymerization (NMRP)

Ober et al. applied NMRP or stable free radical polymerization (SFRP) in the synthesis of MJLCPs. The styrenic monomer 2,5-bis[(4-butylbenzoyl)oxy]styrene (BBOS) polymerizes much faster than styrene in bulk polymerization (Pragliola et al. 1999), which can be attributed to the presence of the LC phase, steric factors, and electronic effect of the acetoxy groups (Gopalan and Ober 2001).



Scheme 3 Synthesis of PMPCS by NMRP (Wan et al. 1999)



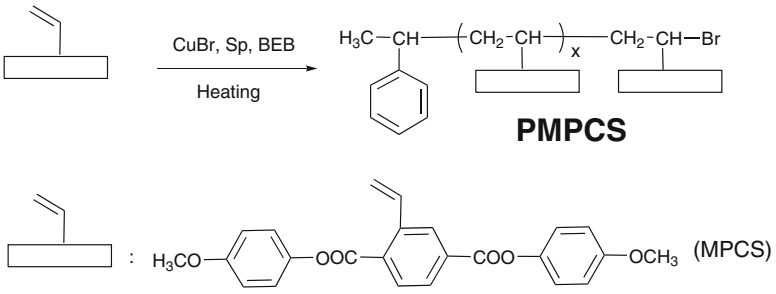
Scheme 4 Synthesis of PMVBP by NMRP (Zhang et al. 2014)

The first synthesis of PMPCS homopolymer using controlled radical polymerization was through TEMPO-mediated NMRP, as shown in Scheme 3 (Wan et al. 1999) with BPO as the initiator, although the synthesis of a block copolymer containing PMPCS was reported earlier. The MW of PMPCS increases almost linearly with increasing conversion during the early stage of polymerization. And the MWD of the resulting polymer is relatively narrow (lower than 1.5). Therefore, the polymerization has certain "living" characteristics. In addition, MPCS also polymerizes much faster than styrene.

Recently we synthesized a new MJLCP, poly(4′-(methoxy)-2-vinylbiphenyl-4-methyl ether) (PMVBP) having a smaller monomer MW using NMRP, as shown in Scheme 4 (Zhang et al. 2014). PMVBP has a relatively high T_g of 173–208 °C. And it has a low threshold MW of 0.53×10^4 Da for the formation of LC phases. The polymer develops a Col_h phase above this threshold MW, and the LC phase remains upon cooling.

Atom Transfer Radical Polymerization (ATRP)

ATRP has been widely used in synthesizing MJLCPs with controlled MWs and MWDs. The first example of applying this method was in the synthesis of PMPCS, as shown in Scheme 5 (Zhang et al. 2002). The polymerization was carried out in methoxybenzene, with 1-bromoethylbenzene (BEB) as the initiator and the complex of CuBr with sparteine (Sp) as the catalyst. The "living" nature during the ATRP of MPCS was confirmed by the first-order kinetics, a linear MW-conversion



Scheme 5 Synthesis of PMPCS by ATRP (Zhang et al. 2002)

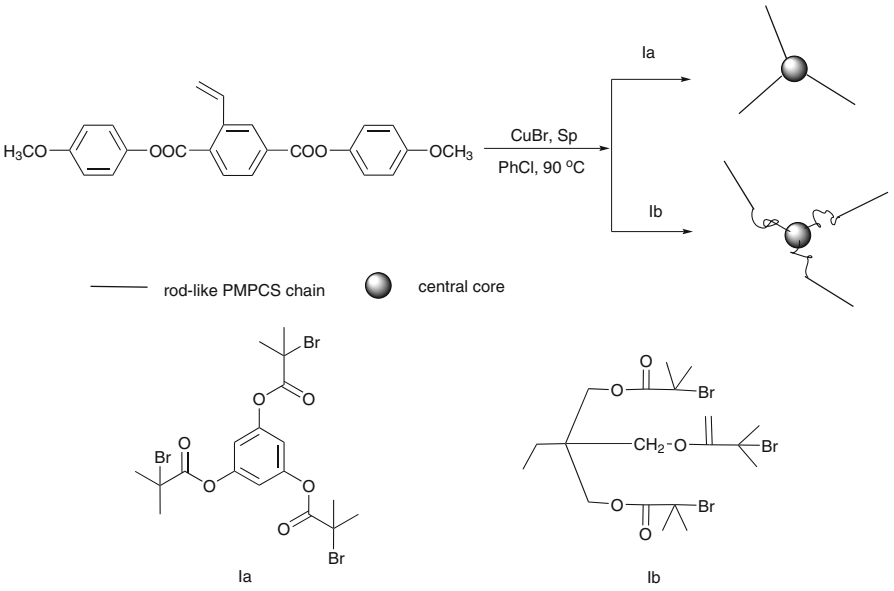
relationship, and a relatively narrow MWD of the resultant polymer. The LC behavior of PMPCS shows a clear MW dependence.

Since then, other MJLCP homopolymers, such as PHPCS (polymer **5** with $n = 6$ in Chart 1), PBPCS (polymer **5** with $n = 4$ in Chart 1), poly[2, 5-(4′-alkoxybiphenyloxycarbonyl) styrene] (P*n*CbiPCS, $n = 4$, 6, 8, 10, 14), and poly{[3,6,7,10,11-pentakis (hexyloxy)-2-oxy-triphenylene]methacrylate} (PMTS), have been successfully synthesized using ATRP. In the polymerizations of these abovementioned MJLCPs, CuBr/PMDETA was used as the catalyst.

In addition, polymers with other architectures, including block copolymers, star polymers, and hyperbranched polymers, can also be prepared by ATRP. For example, by using sequential ATRP, block copolymers containing MJLCP blocks can be readily synthesized. In a recent book chapter, we have summarized the controlled synthesis of MJLCP-containing BCPs. When trifunctional initiators 1,3,5-(2′-bromo-2′-methylpropionato)benzene (Ia) and 1,1,1-tris(2-bromo-isobutyryloxymethyl)propane (Ib) were used, starlike MJLCPs were obtained by ATRP, as shown in Scheme 6 (Wang et al. 2005). The liquid crystalline behavior was found to be independent of the core structure but dependent on the MW of the arm. By using a tetrafunctional initiator, a four-arm star-shaped PMPCS was also synthesized by ATRP.

With octafunctionalized octakis(2-bromo-2-methylpropionoxypropyldimethylsiloxy) octasilsesquioxane (OBPS) as the initiator, an eight-arm star PMPCS was synthesized using ATRP, as shown in Scheme 7 (Pan et al. 2007). The effect of architecture on the LC phase behavior was investigated. By cleaving off the PMPCS arms from the silsesquioxane core using hydrofluoric acid, this star polymer was found to have the precise octafunctionality. Compared to linear PMPCS, the eight-arm star PMPCS shows liquid crystallinity with a lower threshold MW of each arm, and PMPCS is generally packed in a more ordered fashion.

In addition, a branched MJLCP containing PMPCS was obtained by ATRP (Mei et al. 2008). It involves the copolymerization of MPCS and non-mesogenic 4-chloromethyl styrene (CMS). The catalyst is a $CuCl/CuCl_2$/bipyridine complex. The copolymerization mechanism is shown in Scheme 8. CMS acts like an initiator to polymerize MPCS in the early stage of the copolymerization process. Initially the MW of the resultant polymer displays a linear increase with respect to monomer

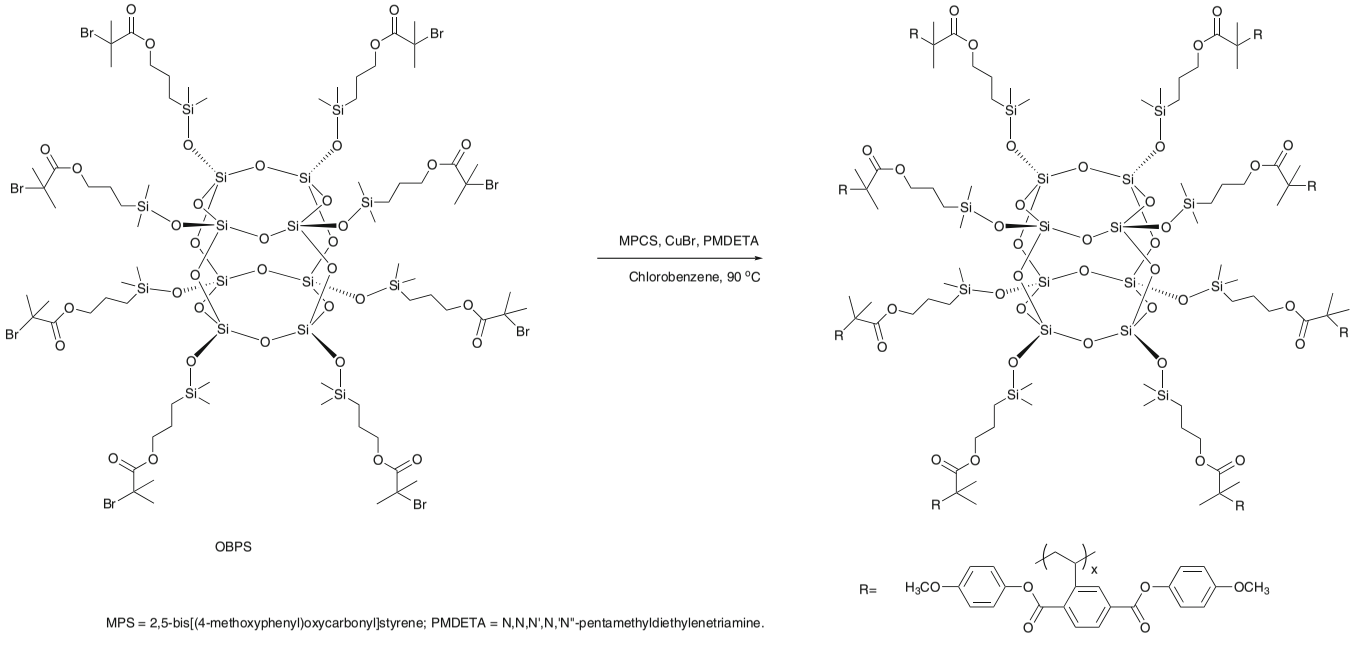


Scheme 6 Synthesis of tri-arm star-shaped PMPCS by ATRP (Wang et al. 2005)

conversion, and the MWD is symmetrical and relatively narrow. With further polymerization, the MWD changes to multimodal, indicating the formation of a branched structure. In order to form a stable LC phase, the MW of the branched PMPCS needs to exceed a minimum value, while the feed molar ratio of MPCS to CMS has to be higher than 30. The branched structure has a depressing effect on liquid crystallinity of PMPCS. As a result, the branched polymer only shows a Col_n phase.

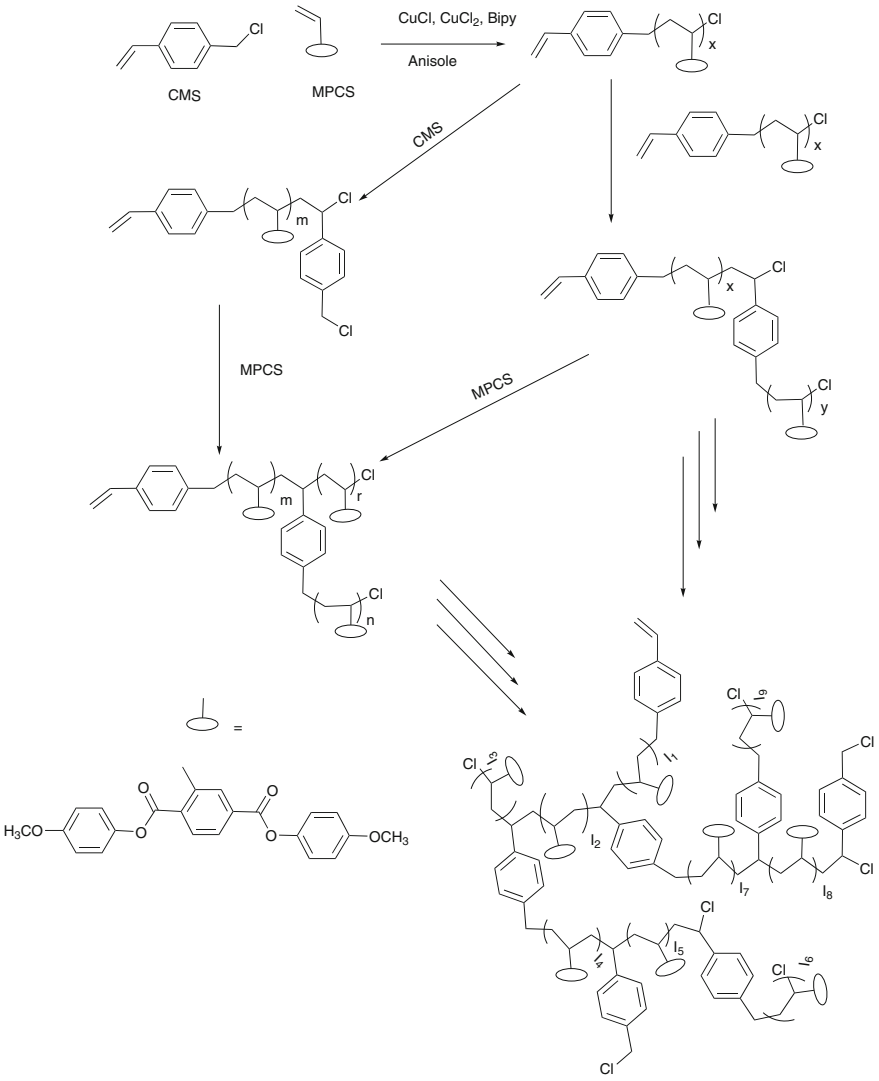
Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

In preparation of water-soluble semirigid thermoresponsive polymers with relatively narrow MWDs, Zhang et al. synthesized a series of MJLCPs, poly[bis (N-hydroxyisopropyl pyrrolidone) 2-vinylterephthalate] (PHIPPVTA), using RAFT polymerization (Liu et al. 2012). The polymers are liquid crystalline when the MW is high enough. The cloud point of the polymer increases with increasing MW, opposite to the trend in flexible thermoresponsive polymers. In addition, the polymer has a lower cloud point in D_2O than in H_2O. Using the similar synthetic approach, they also synthesized three series of MJLCP-based water-soluble thermoresponsive polymers with relatively narrow MWDs, poly[bis(N-(2-hydroxypropyl) pyrrolidone) 2-vinylterephthalate] [P(2-HPPVTA)], poly[bis(N-(1-methyl-2-hydroxyethyl) pyrrolidone) 2-vinylterephthalate] [P(1-M-2-HEPVTA)], and poly[bis (N-hydroxypropyl pyrrolidone) 2-vinylterephthalate] (PHPPVTA) (Liu et al. 2013).



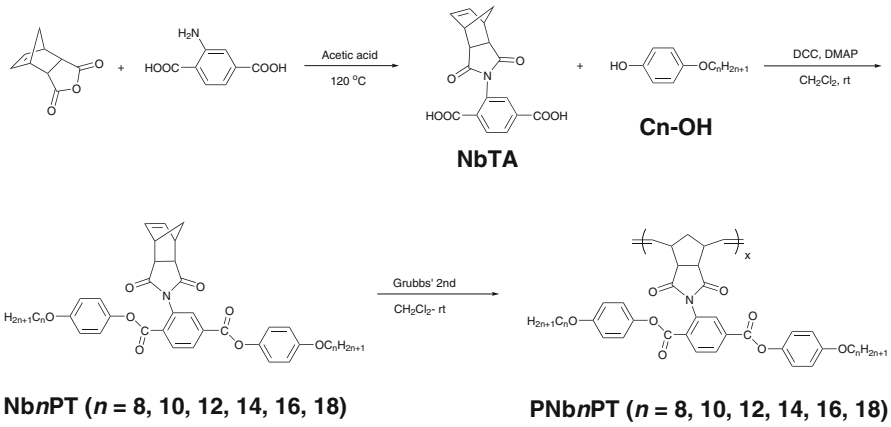
MPS = 2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene; PMDETA = N,N,N',N,'N''-pentamethyldiethylenetriamine.

Scheme 7 Synthesis of eight-arm star-shaped PMPCS by ATRP (Pan et al. 2007)



Scheme 8 Copolymerization mechanism of MPCS and CMS (Mei et al. 2008)

They investigated the effect of steric hindrance on the LC phase behaviors and thermoresponsive behaviors of P(1-M-2-HEPVTA) and P(2-HPPVTA). Although P(1-M-2-HEPVTA) has stronger steric hindrance than that of P(2-HPPVTA), both of the polymers form columnar nematic phases, suggesting little effect on the LC behaviors of the polymers. However, the thermoresponsive behaviors of the two polymers are dependent on the steric hindrance.



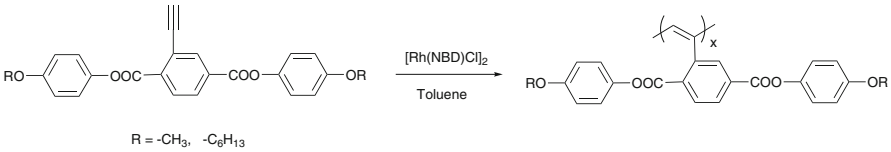
Scheme 9 Synthetic pathway of PNb*n*PTs with a polynorbornene backbone (Zhu et al. 2014b)

Ring-Opening Metathesis Polymerization (ROMP)

Yang and coworkers synthesized MJLCPs with a polynorbornene backbone using the ROMP method (Yang et al. 2013). The mesogen was laterally attached directly to the main chain without spacers. The polymerization was initiated by using a Grubbs catalyst. The polymers are liquid crystalline and exhibit smectic phases when the alkoxy tails of the mesogens are long enough. Recently, we also obtained polynorbornene-based MJLCPs PNb*n*PTs (n = 8, 10, 12, 14, 16, 18, which is the number of carbons in the side-chain alkyl tails) with ROMP (Zhu et al. 2014b). The synthetic procedure is shown in Scheme 9. Similar to the findings of Yang and coworkers, the alkyl-tail length plays an important role in the phase behavior of PNb*n*PT. Only when n = 12, 14, 16, and 18 does PNb*n*PT become liquid crystalline. The LC PNb*n*PTs form SmA phases, with increasing degree of order for polymers with longer alkyl tails. The synthesis of these polynorbornene-based MJLCPs is more robust and more environmentally friendly than those reported by other research groups. Because ROMP has high tolerance of functional groups like fullerene, this convenient synthetic method may be useful to polymerize functionalized monomers, leading to MJLCPs with more functions.

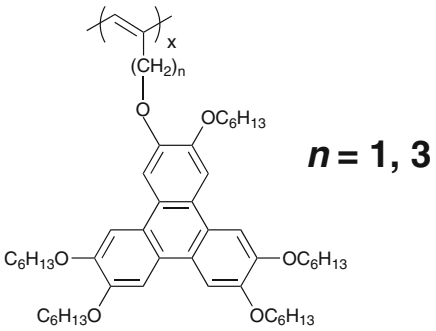
Transition Metal-Catalyzed Metathesis Polymerization

For the synthesis of MJLCPs with a polyacetylene backbone, transition metal-catalyzed metathesis polymerization can be used. As shown in Scheme 10, LC monosubstituted polyacetylenes containing laterally attached side groups without flexible spacers between the side group and the polymer backbone were synthesized by Chen et al. (2006a). The polymerization was performed in toluene using chloronorbornadiene rhodium(I) dimer, $[Rh(NBD)Cl]_2$ (where NBD is



Scheme 10 Synthesis of polyacetylene-based MJLCPs (Chen et al. 2006a)

Chart 5 Chemical structure of polyacetylene-based MJLCP with triphenylene in the side chain

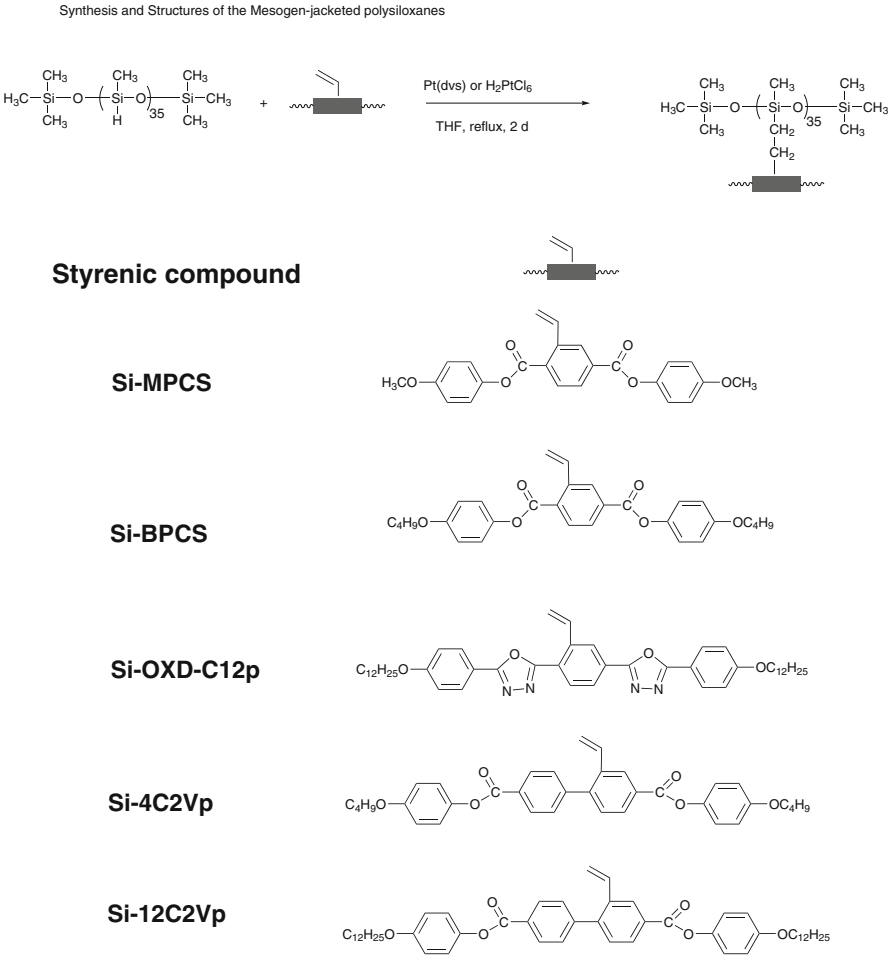


2,5-norbornadiene), as a 1,2-insertion catalyst because the Rh complex catalyst would not be poisoned by the polar ester group. For the two polyacetylenes obtained, only the polymer with a medium length of alkyl tails shows an SmA phase, while the other one with a methyl end group is not liquid crystalline. With the same method using WCl_6-Ph_4Sn catalysts, they also synthesized mesogen-jacketed polyacetylenes containing a terphenyl side-chain core (Peng et al. 2010). A short spacer was introduced to facilitate polymerization. The polymers show enantiotropic SmA phases. Owing to stronger "jacketing" effect of the terphenyl mesogens, the more extended and planar conformation with a better conjugation for the disubstituted polyacetylene leads to the better photoluminescence compared with the mono-substituted polyacetylene.

Recently, Yu et al. successfully synthesized polyacetylene MJLCPs containing a Tp unit and a short spacer in the side chain, as shown in Chart 5, using $[Rh(NBD)Cl]_2$ as the catalyst (Yu et al. 2013). Unlike the mesogen-jacketed polyacetylenes synthesized by Chen et al., these polymers possess a columnar shape and form Col_h phases owing to the introduction of the Tp unit.

Polymer Reaction

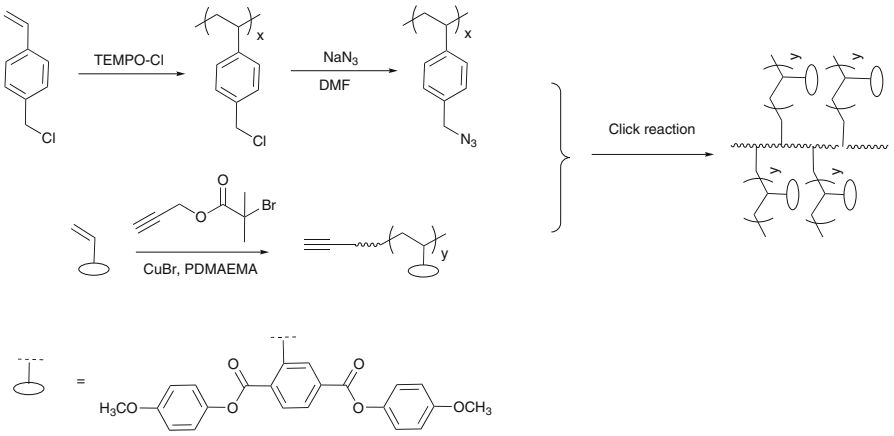
MJLCPs can also be prepared from polymeric precursors through polymer reaction. Polymethylhydrosiloxane can undergo hydrosilylation with the addition of vinyl compounds such as styrenic derivatives. Such a reaction has been employed in the synthesis of conventional SCLCPs. MJLCPs with a short spacer were obtained with this method, as shown in Scheme 11 (Zhang et al. 2010). Although the polysiloxane



Scheme 11 Synthesis of the mesogen-jacketed polysiloxanes (Zhang et al. 2010)

main chain in these MJLCPs is significantly more flexible compared to polystyrene or polyacrylate/polymethacrylate backbones, the polymers still form supramolecular Col_n or smectic LC phases with much narrower temperature ranges of the LC phases. The MJLCPs possess low contact-angle values because the polysiloxane backbone is embedded in the side chains, further confirming the mesogen-jacketed model.

Compared to the general method of polymerizing a monomer, this polymer reaction approach cannot guarantee a 100% reaction efficiency, leading to polymers with chemical defects. Therefore, highly efficient reactions are always preferred. The Cu(I)-catalyzed 1,3-dipolar cycloaddition click reaction was utilized to synthesize a series of comb polymers, poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene}-*g*-polystyrene (PMPCS-*g*-PS), with MJLCP as the side chains from α-yne-terminated



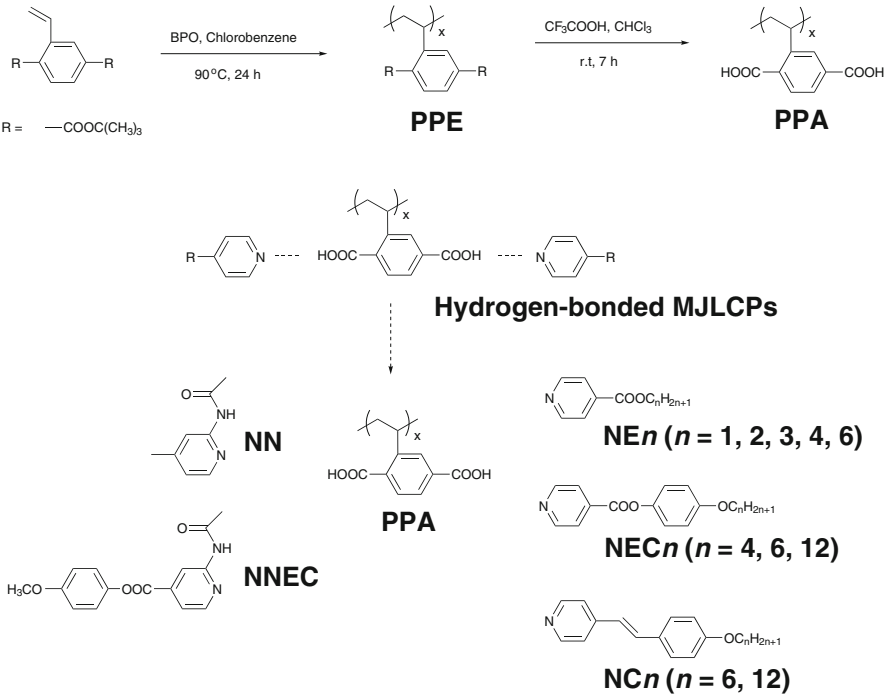
Scheme 12 Synthesis routine of comb polymers with a semirigid MJLCP as side chains (Ma et al. 2012)

PMPCS (side chain) and poly(vinylbenzyl azide) (backbone), as shown in Scheme 12 (Ma et al. 2012). However, the comb polymer did not exhibit liquid crystallinity owing to the confinement of the comb architecture.

Supramolecular Approaches

In addition to chemical reactions, supramolecular strategies have also been employed to obtain MJLCPs. Supramolecular jacketed polymers showing SmA or Col_n LC phases were prepared via hydrogen bonding (Xu et al. 2012). Poly (2-vinylbenzene-1,4-dioic acid) was synthesized and used as the hydrogen-bonding donor, while five series of pyridine derivatives were designed and synthesized as hydrogen-bonding acceptors (Scheme 13). Because the starting polymer is the same, mixing the polymeric hydrogen-bonding donor and acceptors leads to complexes with the same DP and polydispersity, which is advantageous in studying the structure-property relationships of MJLCPs. The structures of the pyridine derivatives, including the rigidity, and the hydrogen-bonding strength are vitally important in determining the LC behaviors of the complexes obtained. The disadvantage of this method lies in the uncertainty of the chemical structures of the complexes, compared to regular MJLCPs synthesized using covalent bonds.

Two mesogen-jacketed liquid crystalline polyelectrolytes (MJPEs), poly{sodium 2,5-bis[(4-sulfophenyl)aminocarbonyl]styrene} (PSPAS) and poly{sodium 2.5-bis [(4-sulfophenyl)oxycarbonyl]-styrene} (PSPCS), with sulfonate groups on the two ends of the side chains were synthesized by conventional radical polymerization. Then, cationic lipids of different lengths and shapes were chosen to complex with these two MJPEs (Scheme 14), leading to comb-shaped nonstoichiometric polymer-surfactant complexes (Cheng et al. 2011b). The length and shape of the lipids

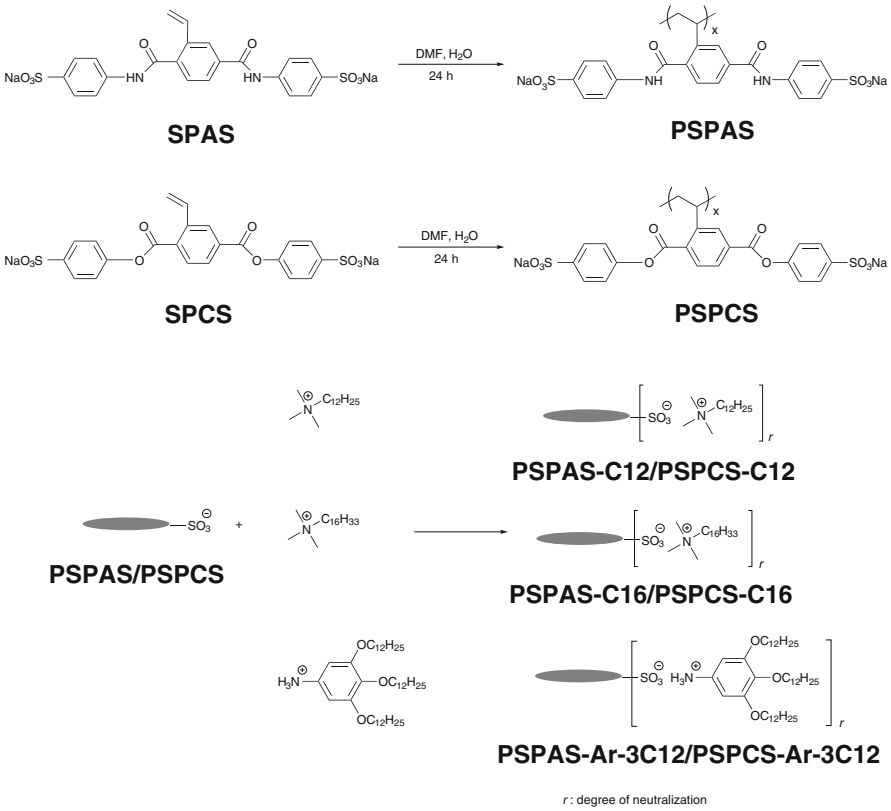


Scheme 13 Preparation of MJLCPs by hydrogen bonding (Xu et al. 2012)

strongly influence the structures of the complexes. The complexes formed by the two polyelectrolytes with cetyltrimethylammonium bromide with a longer alkyl tail and the fan-shaped 3,4,5-tris(dodecyloxy)-benzenamine exhibit lamellar structures. In these complexes, the chemical structure of the backbone does not show a significant influence on the phase behavior because the stronger electrostatic interactions overwhelm the hydrogen bonding in PSPAS and dominate the self-assembling process.

Future Directions

Although a lot of research has been done in the synthesis and phase behavior study of MJLCPs, there are still many challenges. To address these challenges, more work can be carried out in the following aspects in the future: (1) design of monomers which can be more easily synthesized and polymerized, (2) cost- and time-saving synthetic methods, (3) calculation and computer simulation which can accurately predict phase behaviors and guide molecular design, and (4) functional materials based on MJLCPs for practical applications.



Scheme 14 Preparation of MJLCPs by ionic interaction (Cheng et al. 2011b)

References

Chai CP, Zhu XQ, Wang P, Ren MQ, Chen XF, Xu YD, Fan XH, Ye C, Chen EQ, Zhou QF (2007) Synthesis and phase structures of mesogen-jacketed liquid crystalline polymers containing 1,3,4-oxadiazole based side chains. Macromolecules 40:9361–9370

Chen L, Chen YW, Zha DJ, Yang Y (2006a) Synthesis and properties of polyacetylenes with directly attached bis(4-alkoxyphenyl)terephthalate mesogens as pendants. J Polym Sci Part A Polym Chem 44:2499–2509

Chen XF, Tenneti KK, Li CY, Bai YW, Zhou R, Wan XH, Fan XH, Zhou QF (2006b) Design, synthesis, and characterization of bent-core mesogen-jacketed liquid crystalline polymers. Macromolecules 39:517–527

Chen S, Gao LC, Zhao XD, Chen XF, Fan XH, Xie PY, Zhou QF (2007) Synthesis and properties of mesogen-jacketed liquid crystalline polymers with asymmetry mesogenic core. Macromolecules 40:5718–5725

Chen S, Zhang L-Y, Gao L-C, Chen X-F, Fan X-H, Shen Z, Zhou Q-F (2009) Influence of alkoxy tail length and unbalanced mesogenic core on phase behavior of mesogen-jacketed liquid crystalline polymers. J Polym Sci Part A Polym Chem 47:505–514

Chen X-F, Shen Z, Wan X-H, Fan X-H, Chen E-Q, Ma Y, Zhou Q-F (2010) Mesogen-jacketed liquid crystalline polymers. Chem Soc Rev 39:3072–3101

Cheng YH, Chen WP, Shen Z, Fan XH, Zhu MF, Zhou QF (2011a) Influences of hydrogen bonding and peripheral chain length on Mesophase structures of Mesogen-jacketed liquid crystalline polymers with amide side-chain linkages. Macromolecules 44:1429–1437

Cheng YH, Chen WP, Zheng C, Qu W, Wu HL, Shen ZH, Liang DH, Fan XH, Zhu MF, Zhou QF (2011b) Synthesis and phase structures of Mesogen-jacketed liquid crystalline polyelectrolytes and their ionic complexes. Macromolecules 44:3973–3980

Cui JX, Lu XC, Liu AH, Wan XH, Zhou QF (2009) Long-range chirality transfer in free radical polymerization of bulky vinyl monomers containing laterally attached p-Terphenyl groups. Macromolecules 42:7678–7688

Cui JX, Liu AH, Cao HQ, Wan XH, Zhou QF (2010) Unusual chiral transfer in radical copolymerization of vinyl monomers bearing side-on p-Terphenyl pendants. Chemistry-an Asian J 5:1139–1145

Finkelmann H, Ringsdorf H, Wendorff JH (1978) Model considerations and examples of enantiotropic liquid-crystalline polymers – Polyreactions in ordered systems. 14. Makromol Chem-Macromol Chem Phys 179:273–276

Gao L-C, Fan X-H, Shen Z-H, Chen X, Zhou Q-F (2009) Jacketed polymers: controlled synthesis of mesogen-jacketed polymers and block copolymers. J Polym Sci Part A Polym Chem 47:319–330

Gopalan P, Ober CK (2001) Highly reactive 2,5-disubstituted styrene-based monomer polymerized via stable free radical polymerization: effect of substitution and liquid crystallinity on polymerization. Macromolecules 34:5120–5124

Gopalan P, Andruzzi L, Li XF, Ober CK (2002) Fluorinated mesogen-jacketed liquid-crystalline polymers as surface-modifying agents: design, synthesis and characterization. Macromol Chem Phys 203:1573–1583

Hardouin F, Mery S, Achard MF, Noirez L, Keller P (1991) Evidence for a jacketed nematic polymer. J Phys II 1:511–520

Hardouin F, Leroux N, Mery S, Noirez L (1992) Small-angle neutron-scattering experiments on side-on fixed liquid –crystal polysiloxanes. J Phys II 2:271–278

Hessel F, Finkelmann H (1985) A new class of liquid-crystal side-chain polymers – mesogenic groups laterally attached to the polymer backbone. Polym Bull 14:375–378

Hessel F, Finkelmann H (1986) Optical biaxiality of nematic LC-side chain polymers with laterally attached mesogenic groups. Polym Bull 15:349–352

Jin H, Xu YD, Shen ZH, Zou DC, Wang D, Zhang W, Fan XH, Zhou QF (2010) Jacketed polymers with dendritic carbazole side groups and their applications in blue light-emitting diodes. Macromolecules 43:8468–8478

Lin JP (1997) Re-entrant isotropic transition of polypeptide liquid crystal. Polymer 38:4837–4841

Liu P, Xie H, Tang H, Zhong G, Zhang H (2012) Unusual effect of molecular weight and concentration on thermoresponsive behaviors of well-defined water-soluble semirigid polymers. J Polym Sci Part A Polym Chem 50:3664–3673

Liu P, Tan Q, Xiang L, Zhang H (2013) Steric hindrance effect on thermo-responsive behaviors of well-defined water-soluble semi-rigid polymers. J Polym Sci Part A Polym Chem 51:3429–3438

Ma ZY, Zheng C, Shen ZH, Liang DH, Fan XH (2012) Synthesis and properties of comb polymers with semirigid mesogen-jacketed polymers as side chains. J Polym Sci Part A Polym Chem 50:918–926

McArdle CB (1989) Side chain liquid crystal polymers. Blackie and Son Ltd, Glasgow

Mei X, Liu AH, Cui JX, Wan XH, Zhou QF (2008) Synthesis and characterization of branched mesogen-jacketed liquid crystal polymers based on 2,5-bis[(4-methoxyphenyl)oxycarbonyl] styrene and 4-chloromethylstyrene. Macromolecules 41:1264–1272

Mei X, Chu Y, Cui J, Shen Z, Wan X (2010) Steric interaction between flexible main chain and nonmesogenic cyclic pendants leading to thermotropic liquid crystalline property. Macromolecules 43:8942–8949

Mei X, Zhang J, Shen ZH, Wan XH (2012) Synthesis, liquid crystalline properties, and lithium complexes of vinyl polymers with cyclic pendants containing ethylene oxide units. Polym Chem 3:2857–2866

Pan QW, Gao LC, Chen XF, Fan XH, Zhou QF (2007) Star mesogen-jacketed liquid crystalline polymers with silsesquioxane core: synthesis and characterization. Macromolecules 40:4887–4894

Papkov VS, Ilina MN, Zhukov VP, Tsvankin DJ, Tur DR (1992) UNUSUAL PHASE-BEHAVIOR OF SOME POLY(DIALKOXYPHOSPHAZENES). Macromolecules 25:2033–2040

Peng H, Chen Y, Chen L, He X, Li F (2010) Luminescent Mesogen jacketed poly(1-alkyne) bearing lateral Terphenyl with Hexyloxy tail. J Polym Sci Part A Polym Chem 48:5679–5692

Percec V, Tomazos D (1992) Molecular engineering of side-chain liquid-crystalline polymers by living cationic polymerization. Adv Mater 4:548–561

Pragliola S, Ober CK, Mather PT, Jeon HG (1999) Mesogen-jacketed liquid crystalline polymers via stable free radical polymerization. Macromol Chem Phys 200:2338–2344

Pugh C, Schrock RR (1992) Synthesis of side-chain liquid-crystal polymers by living ring-opening metathesis polymerization. 3. Influence of molecular-weight, interconnecting unit, and substituent on the mesomorphic behavior of polymers with laterally attached mesogens. Macromolecules 25:6593–6604

Qu W, Zhu XQ, Chen JH, Niu L, Liang DH, Fan XH, Shen ZH, Zhou QF (2014) Synthesis and characterization of a Mesogen-jacketed polyelectrolyte. Macromolecules 47:2727–2735

Rosen BM, Wilson CJ, Wilson DA, Peterca M, Imam MR, Percec V (2009) Dendron-mediated self-assembly, disassembly, and self-organization of complex systems. Chem Rev 109:6275–6540

Rudick JG, Percec V (2008) Induced helical backbone conformations of self-organizable dendronized polymers. Acc Chem Res 41:1641–1652

Tu HL, Zhang D, Wan XH, Chen XF, Liu YX, Zhang HL, Zhou QF (1999) Mesogen-jacketed liquid crystalline polymer with flexible dicyclopentyl terephthalate as side group. Macromol Rapid Commun 20:549–551

Tu HL, Wan XH, Liu YX, Chen XF, Zhang D, Zhou QF, Shen ZH, Ge JJ, Jin S, Cheng SZD (2000) Self-assembly-induced supramolecular hexagonal columnar liquid crystalline phase using laterally attached nonmesogenic templates. Macromolecules 33:6315–6320

Wan XH, Zhang F, Wu PQ, Zhang D, Feng XD, Zhou QF (1995) Characterization of the chain stiffness for a mesogen-jacketed liquid-crystal polymer – poly(2,5-bis[(4-methoxybenzoyl)oxy] styrene). Macromol Symp 96:207–218

Wan XH, Tu HL, Tu YF, Zhang D, Sun L, Zhou QF, Dong YP, Tang M (1999) Nitroxide-mediated free radical synthesis of mesogen-jacketed liquid crystal polymers. Chin J Polym Sci 17:189–192

Wang X-J, Zhou Q-F (2004) Liquid crystalline polymers. World Scientific Publishing Co. Pte. Ltd, Singapore

Wang XZ, Zhang HL, Shi DC, Chen JF, Wang XY, Zhou QF (2005) Synthesis of a novel star liquid crystal polymer using trifunctional initiator via atom transfer radical polymerization. Eur Polym J 41:933–940

Xu GZ, Wu W, Shen DY, Hou JN, Zhang SF, Xu M, Zhou QF (1993a) Morphological-study of oriented films obtained from side-chain liquid-crystalline polymers. Polymer 34:1818–1822

Xu GZ, Wu W, Xu M, Zhou QF (1993b) Banded texture in oriented films of a side-chain liquid-crystalline polymer. J Polym Sci B Polym Phys 31:229–230

Xu YD, Yang Q, Shen ZH, Chen XF, Fan XH, Zhou QF (2009) Effects of mesogenic shape and flexibility on the phase structures of mesogen-jacketed liquid crystalline polymers with bent side groups containing 1,3,4-oxadiazole. Macromolecules 42:2542–2550

Xu YD, Qu W, Yang Q, Zheng JK, Shen ZH, Fan XH, Zhou QF (2012) Synthesis and characterization of mesogen-jacketed liquid crystalline polymers through hydrogen-bonding. Macromolecules 45:2682–2689

Yang Q, Jin H, Xu YD, Wang P, Liang XC, Shen ZH, Chen XF, Zou DC, Fan XH, Zhou QF (2009) Synthesis, photophysics, and electroluminescence of mesogen-jacketed 2D conjugated copolymers based on fluorene-thiophene-oxadiazole derivative. Macromolecules 42:1037–1046

Yang H, Zhang F, Lin B-P, Keller P, Zhang X-Q, Sun Y, Guo L-X (2013) Mesogen-jacketed liquid crystalline polymers and elastomers bearing polynorbornene backbone. J Mater Chem C 1:1482–1490

Ye C, Zhang HL, Huang Y, Chen EQ, Lu YL, Shen DY, Wan XH, Shen ZH, Cheng SZD, Zhou QF (2004) Molecular weight dependence of phase structures and transitions of mesogen-jacketed liquid crystalline polymers based on 2-vinylterephthalic acids. Macromolecules 37:7188–7196

Yin XY, Ye C, Ma X, Chen EQ, Qi XY, Duan XF, Wan XH, Cheng SZD, Zhou QF (2003) Manipulating supramolecular self-assembly via tailoring pendant group size of linear vinyl polymers. J Am Chem Soc 125:6854–6855

Yu ZN, Wan XH, Tu HL, Chen XF, Zhou QF (2003a) A novel thermotropic behavior of a mesogen-jacketed liquid crystal polymer. Acta Polym Sin:430–433

Yu ZN, Wan XH, Zhang HL, Chen XF, Zhou QF (2003b) A free radical initiated optically active vinyl polymer with memory of chirality after removal of the inducing stereogenic center. Chem Commun:974–975

Yu ZQ, Lam JWY, Zhao KQ, Zhu CZ, Yang S, Lin JS, Li BS, Liu JH, Chen EQ, Tang BZ (2013) Mesogen jacketed liquid crystalline polyacetylene containing triphenylene discogen: synthesis and phase structure. Polym Chem 4:996–1005

Zhang D, Liu YX, Wan XH, Zhou QF (1999) Synthesis of a new side-chain type liquid crystal polymer poly[dicyclohexyl vinylterephthalate]. Macromolecules 32:4494–4496

Zhang H, Yu Z, Wan X, Zhou QF, Woo EM (2002) Effects of molecular weight on liquid-crystalline behavior of a mesogen-jacketed liquid crystal polymer synthesized by atom transfer radical polymerization. Polymer 43:2357–2361

Zhang LY, Chen S, Zhao H, Shen ZH, Chen XF, Fan XH, Zhou QF (2010) Synthesis and properties of a series of mesogen-jacketed liquid crystalline polymers with polysiloxane backbones. Macromolecules 43:6024–6032

Zhang Q-K, Tian H-J, Li C-F, Zhu Y-F, Liang Y, Shen Z, Fan X-H (2014) Synthesis and phase behavior of a new 2-vinylbiphenyl-based mesogen-jacketed liquid crystalline polymer with high glass transition temperature and low threshold molecular weight. Polym Chem 5:4526–4533

Zhao YF, Fan XH, Wan XH, Chen XF, Yi Y, Wang LS, Dong X, Zhou QF (2006) Unusual phase behavior of a mesogen-jacketed liquid crystalline polymer synthesized by atom transfer radical polymerization. Macromolecules 39:948–956

Zhou QF, Li HM, Feng XD (1987) Synthesis of liquid-crystalline polyacrylates with laterally substituted mesogens. Macromolecules 20:233–234

Zhou QF, Zhu XL, Wen ZQ (1989) Liquid-crystalline side-chain polymers without flexible spacer. Macromolecules 22:491–493

Zhou QF, Wan XH, Zhu XL, Zhang F, Feng XD (1993) Restudy of the old poly-2,5-di(benzoyloxy) styrene as a new liquid-crystal polymer. Mol Cryst Liq Cryst 231:107–117

Zhu YF, Guan XL, Shen ZH, Fan XH, Zhou QF (2012) Competition and promotion between two different liquid-crystalline building blocks: Mesogen-jacketed liquid-crystalline polymers and triphenylene discotic liquid crystals. Macromolecules 45:3346–3355

Zhu YF, Tian HJ, Wu HW, Hao DZ, Zhou Y, Shen ZH, Zou DC, Sun PC, Fan XH, Zhou QF (2014a) Ordered nanostructures at two different length scales mediated by temperature: a triphenylene-containing mesogen-jacketed liquid crystalline polymer with a long spacer. J Polym Sci Part A Polym Chem 52:295–304

Zhu YF, Zhang ZY, Zhang QK, Hou PP, Hao DZ, Qiao YY, Shen ZH, Fan XH, Zhou QF (2014b) Mesogen-jacketed liquid crystalline polymers with a polynorbornene main chain: green synthesis and phase behaviors. Macromolecules 47:2803–2810

Zhu YF, Liu W, Zhang MY, Zhou Y, Zhang YD, Hou PP, Pan Y, Shen ZH, Fan XH, Zhou QF (2015) POSS-containing jacketed polymer: hybrid inclusion complex with hierarchically ordered structures at sub-10 nm and angstrom length scales. Macromolecules 48:2358–2366