Chapter 5
Side-Chain Liquid Crystalline Polymers: Controlled Synthesis and Hierarchical Structure Characterization

Shi Pan, Bin Mu, Bin Wu, Zehua Shi, and Dongzhong Chen

5.1 General Introduction

Liquid crystalline polymers (LCPs) represent a kind of advanced organic functional materials combining both anisotropic order of liquid crystal and excellent mechanical properties of polymer. Study on LCPs has been a flourishing research field due to their broad promising applications in various high-technology areas such as various organic optoelectronic applications, non-linear optical materials, tunable diffraction gratings, thermal insulated materials, and the high performance Kevlar fiber. It's convenient to divide LCPs into several general categories based on their architecture and position of mesogens in the polymer chain. Generally speaking, mesogens can be introduced as building blocks in main chain, as side groups or acting as cross linkers, to form main-chain LCPs, side-chain LCPs or LCP networks/elastomers respectively, as shown in Fig. 5.1. Side-chain LCPs have developed steadily ever since the innovative "spacer decoupling principle" suggested by Finkelmann et al. (1978a, b).

Certainly, some further detailed classification can be subdivided. For side-chain LCPs, end-on and side-on types are called according to their linking site of mesogenic units to the polymer backbone, longitudinally at the end or laterally in the middle of mesogens. Moreover, if very short spacers were adopted or no spacers for side-on type attachment, a dense "jacket" would surround the partially extended polymer backbone (Wang and Zhou 2004). Such type of LCPs was pioneered by Zhou et al. and given the name of "mesogen-jacketed liquid crystalline polymer (MJLCP)" (Chen et al. 2010; Zhou et al. 1987). Note that the subdivision of end-on and side-on types is based on calamitic or bent-core mesogen units, while as for

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S. Pan • B. Mu • B. Wu • Z. Shi • D. Chen (✉)
Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Key Laboratory of High Performance Polymer Materials and Technology of Ministry of Education, Nanjing University, 22 Hankou Road, Nanjing 210093, China
e-mail: cdz@nju.edu.cn

V.K. Thakur, M.R. Kessler (eds.), *Liquid Crystalline Polymers*,
DOI 10.1007/978-3-319-22894-5_5

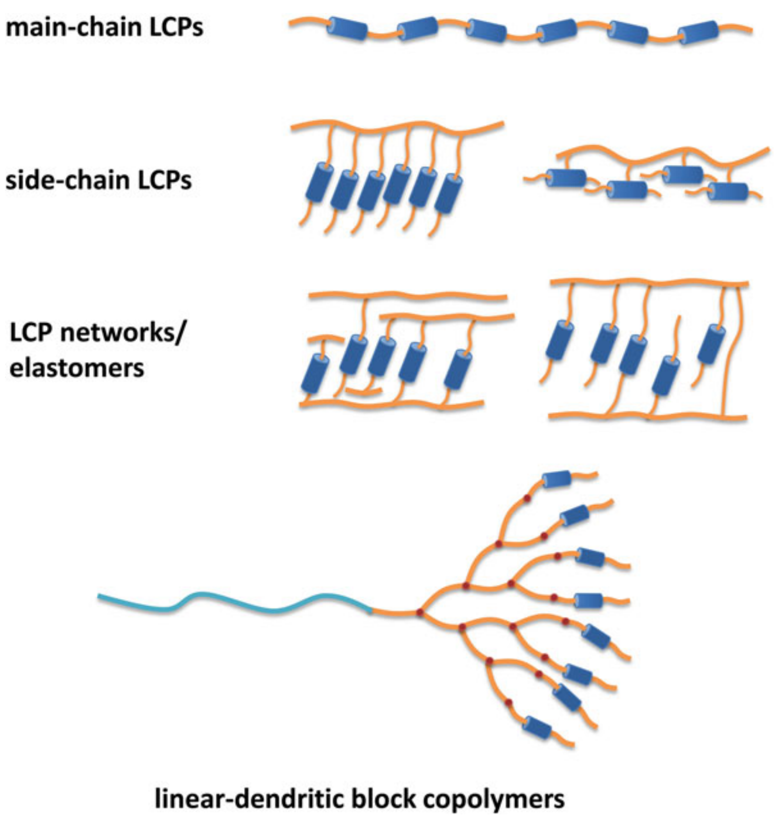

Fig. 5.1 Some liquid crystalline polymer (LCP) categories based on calamitic mesogens: main-chain LCPs, side-chain LCPs, LCP networks/elastomers and linear–dendritic block copolymers (LDBCs) with side-chain type dendritic segments

discotic LCPs, usually there is no such classification considering the geometry of disc-like mesogenic units, except for some extremely special occasions (Zhu et al. 2012, 2014).

These categories may also overlap on some occasions. For instance, liquid crystal elastomers (LCEs) combine anisotropic characteristics of LC phases and elasticity of polymer networks (Ikeda et al. 2007). The key character of chemistry structure for LCEs is their lightly cross-linked network system, which implies that they also possess some common features of LCPs. Also, the combined main-chain/side-chain liquid crystalline polymers have been studied in depth (Demus et al. 1998; Ge et al. 1997; Zhou and Han 2005), showing some interesting LC properties for their comprehensive nature comprising main-chain and side-chain LCPs.

On the other hand, LCPs can also be classified by their mesogenic orders. Nematic, smectic and cholesteric LCPs can be categorized in this way, according to specific orientation and positional order. In this Chapter, we shall mainly employ the classification based on type and location of mesogens rather than mesogenic orders.

Main-chain LCPs are usually obtained via stepwise polymerization. The mesogenic units in polymer backbone exhibit a strong tendency of orientation along the chain axis. Nowadays, many industrialized main-chain LCPs have been developed for high-performance materials with wide applications. The wholly aromatic polyamides, prepared by elaborate linear condensation polymerization, are representative main-chain LCPs showing lyotropic liquid crystalline order. Among them, poly-paraphenylene diamine terephthalamide is probably the most famous synthetic fiber, commonly known as "Kevlar". The wholly aromatic polyesters are another kind of typical thermotropic main-chain LCPs widely used as high performance polymer materials. Considering the general theme of this Chapter, main-chain LCPs will not be covered in the following content.

The controlled synthesis and hierarchical structure investigations of side-chain LCPs constitute the primary topics in this Chapter. The introduction of dendritic segments is a fantastic idea in molecular designing of LCPs, for their ordered supramolecular assembly capabilities can considerably enhance the functionality of LCPs and provide particular scaffolds for creation of novel LC materials (Donnio et al. 2007). Dendritic polymers fall into three categories: dendrimers/dendrons, hyperbranched polymers, dendronized polymers. Dendrimers and dendrons can be regarded as ideal branched polymers, wherein each repeat unit introduces a new AB_n multifunctional moiety (Rosen et al. 2009). So in this chapter, besides "ordinary" side-chain LCPs, side-chain liquid crystalline dendrimers especially linear–dendritic block copolymers (LDBCs) will also be briefly reviewed.

Liquid crystalline (LC) dendrimers can also be classified according to the locations of mesogen units. Thus, main-chain and side-chain LC dendrimers are proposed analogously. Side-chain LC dendrimers possess an overall structure generally consists of mesogenic or pro-mesogenic units attached on the branch terminals of the flexible dendritic network (Donnio et al. 2007; Donnio and Guillon 2006), which can be further divided into end-on and side-on types based on the linking site of mesogenic units. Main-chain LC dendrimers, on the other hand, have their mesogenic units located at every level of the dendritic hierarchy (Donnio et al. 2007). Restricted by the Chapter space, systematic introduction of liquid crystalline dendrimers is not allowed here. Interested readers are suggested to read the thorough review by Rosen et al. (2009). In this Chapter, liquid crystalline LDBCs (as shown in Fig. 5.1) composed of a linear polymer chain and a LC dendritic block will be concisely reviewed.

We shall not try to cover every corner of side-chain LCPs in this Chapter, and the main theme of this Chapter will be a combination of controlled synthesis, rational molecular design and hierarchical organization behaviors, mainly based on two kinds of widely used mesogenic units of calamitic azobenzene (AZO) and discotic triphenylene (TP) derivatives. Some recent progress on liquid crystalline block copolymers based on side-chain LCPs, including linear–dendritic block copolymers, will be briefly summarized. We hope that the summary and some comments put forward here will help to stimulate and promote the sustained and extensive research in side-chain LCPs and related fields.

5.2 Side-Chain LCPs Based on Calamitic and Discotic Mesogens

Side-chain LCPs usually comprise several structural motifs: the polymer backbone, the spacer (the connecting moiety) and the mesogen units (Wang and Zhou 2004). The linking or anchoring group and the number of mesogens per repeat unit ("mesogen density") are some additional factors for the design and synthesis of side-chain LCPs (Trimmel et al. 2005).

The strong tendency to form random coil comformations of the flexible main chain (backbone) conflicts with the anisotropic ordering organization of the attached side-chain mesogenic units. Therefore in order to achieve LC phases, it seems the key point is to reconcile the contradiction between the polymer backbone and side-chain mesogens. In 1978, Finkelmann et al. (1978a, b) proposed the deeply influential "spacer decoupling principle"— flexible spacers between main chain and rigid mesogens to decouple the interference for allowing the mesogenic units to take preferable orientations and realize well organization. Since then, syntheses of side-chain LCPs have been mostly complying with this classical principle, and variant length spacers have been employed for the formation and retaining of liquid crystalline phases in side-chain LCPs (Demus et al. 1998; Wang and Zhou 2004). In some cases, the influence of spacer type and length on LC phases is complicated. For example, Gemmell et al. (1985) reported large differences in the thermal stability of smectic phases in side-chain LCPs with an even or odd number of methylene groups. Recently, Wang and Wang (2010) carried out a detailed theoretical study on the spacer conformation of side-chain LCPs. Generally, as the flexibility of polymer backbone increases, the glass transition temperature usually decreases, while the corresponding isotropization temperature increases (Demus et al. 1998). However, Shibaev et al (1982) reported that in some specific cases with polyacrylate and polymethacrylate main chain, when flexible spacers were introduced between the main chain and the mesogens, their mesophases and transition temperatures were almost unchanged.

Different shape mesogens as shown in Fig. 5.2 are employed in side-chain LCPs. Among them, the most commonly used types in the construction of side-chain LCPs are the calamitic and discotic mesogens, which are also the types of mesogens primarily employed in our laboratory such as azobenzene and triphenylene derivatives. Therefore in this Chapter, we shall concentrate on side-chain LCPs bearing these two types of mesogens. For LCPs built with other kinds of side-chain mesogens such as sanidic (boardlike) and bent-core (banana-shaped), interested readers can refer to some critical review publications such as by Reddy and Tschierske (2006) and Voigt-Martin et al. (1995).

Calamitic mesogens hold the overwhelming dominance in side-chain LCPs, accordingly various molecular structures have been developed so far. Because of the simplicity, appropriate rigidity and dimensions, biphenyl derivatives are one of the most commonly used calamitic mesogens. One can expect that composition and structure of mesogens will largely determine the LC properties of side-chain LCPs,

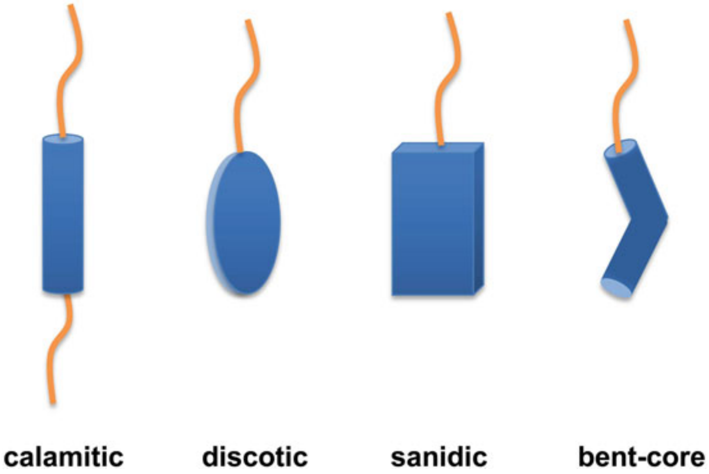

Fig. 5.2 Sketching of different shape mesogenic units used in side-chain LCPs

so variant modifications have been applied to the biphenyl core such as introducing electronwithdrawing groups (Akiyama et al. 1999), prolonged mesogen skeleton (Kumar et al. 2007), chiral centers (Hsiue et al. 2001) and cholesterol groups (Scheerder et al. 2000) (Fig. 5.3a–d). Relatively simple calamitic mesogen units like (a) in Fig. 5.3 usually rendered smetic or nematic phases, and substitution on the end with longer linear alkyl or alkoxy groups favored the formation of smectic phases (Wang and Zhou 2004). The mesogens shown in Fig. 5.3b not only extended the rigid core length, but also introduced photo-crosslinkable vinyl junctions. Mesogen units modified with halogen-containing chiral centres offered side-chain LCPs ferroelectric properties (c in Fig. 5.3), which usually showed a typical smetic C* phase (Beyer et al. 2007; Ikeda et al. 1993).

Research on side-chain LCPs with calamitic mesogens of azobenzene derivatives has been one of the most active research fields in liquid crystals and functional polymer materials. The rigid structure with a large aspect ratio makes azobenzene a classical calamitic mesogen, which is even more attractive than above mentioned biphenyl derivatives. More importantly, the reversible photo-isomerization and light-induced orientation ability of azobenzene derivatives endow their liquid crystalline polymers with fascinating applications, such as functioning as photo-mechanical materials (Beyer et al. 2007; Ikeda et al. 1993), holographic optical storage and surface patterning (Matharu et al. 2007; Natansohn and Rochon 2002), light-controllable micelles/vesicles (Wang and Wang 2013; Zhao and Ikeda 2009), light-controllable LB films (Zou et al. 2010). In fact, azobenzenes have long been used as organic chromophores for optical switching applications as a T-type photochromic system: the photogenerated isomer thermally reverts to its initial form. These photo reactions may affect some other physicochemical properties, such as redox potential, fluorescent intensity, acid/base strength, dielectric constant, dipolar moment, and molecular shape (García-Amorós and Velasco 2012).

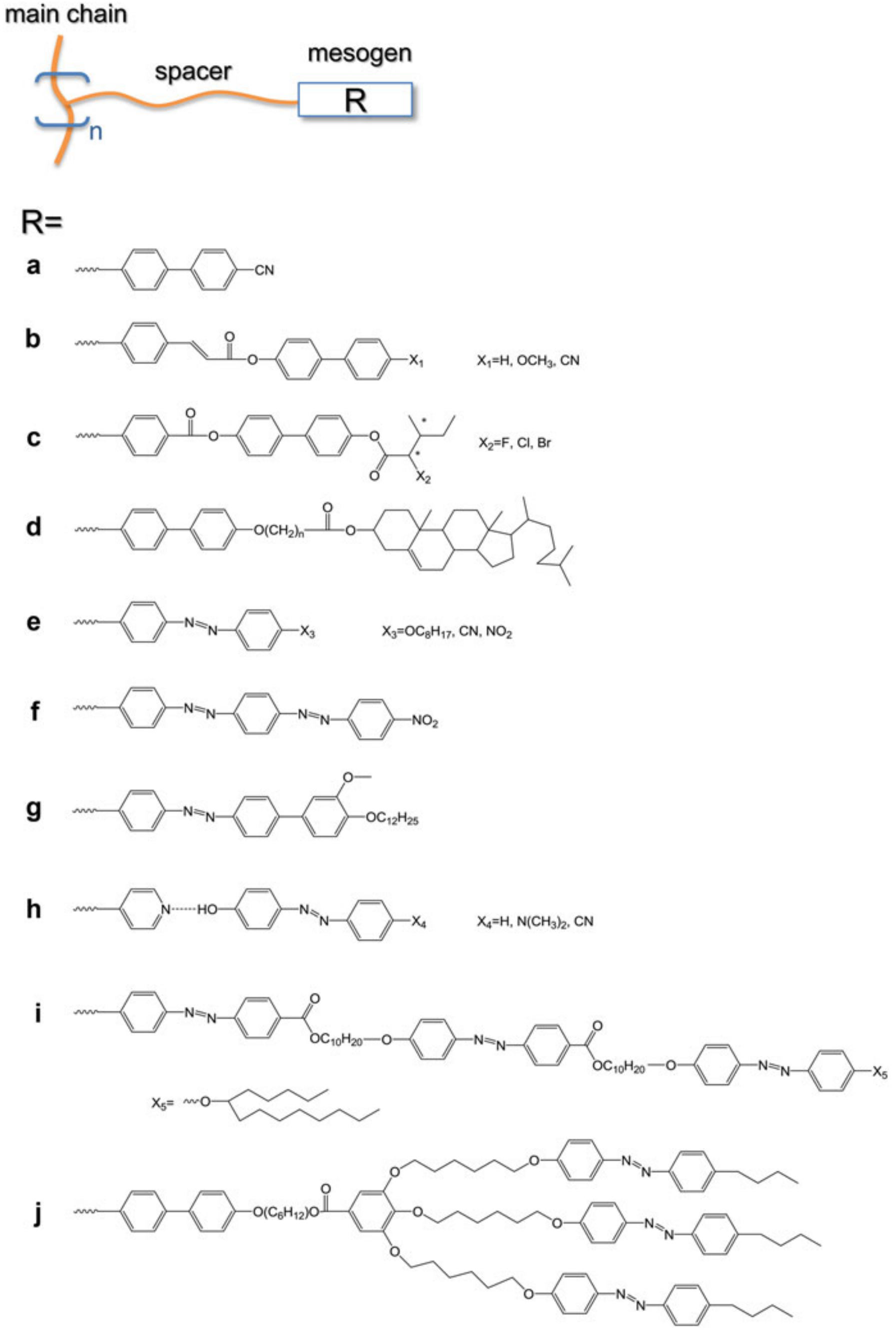

Fig. 5.3 Several typical calamitic mesogens derived from biphenyl or azobenzene rigid cores for side-chain LCPs, and the details of the polymer backbone and spacers are omitted for clarity

Moreover, hardly any side reactions occurred in the photo-isomerization process of azobenzene chromophores and the timescale ranges from microseconds down to sub-nanoseconds, with 10^5–10^6 times reversible cycles before fatigue (Goulet Hanssens and Barrett 2013).

Generally, azobenzene derivatives fall into three basic categories: azobenzene-type molecules, aminoazobenzene-type molecules, and pseudo-stilbenes ("push-pull"). From the first type to the last one, they are characterized by the decreasing of thermal relaxation time in *cis* → *trans* isomerization, and the absorption wavelength red shift for inducing the *trans* → *cis* isomerization. This variation in properties offers azobenzene based LCPs significant advantages over other side-chain LCPs. For instance, π–π^* absorption of pseudo-stilbene chromophores shifts to lower energy toward the red even over the n–π^* absorption (Zhao and Ikeda 2009). Therefore, pseudo-stilbene-containing LCPs are more sensitive to local environment, enabling better photoinduced anisotropy, surface-relief-grating (SRG) formation, and nonlinear optical (NLO) properties (Wang et al. 2009). Yu et al. (2006a) reported a new liquid crystalline block copolymer based on pseudo-stilbene type azobenzene with a cyano group, showing much enhanced photo-orientation ability. It is fairly convenient to obtain a wide variety of azobenzene chromophore based molecular architectures with facile anchoring and modifications (Mahimwalla et al. 2012) as briefly gathered in Fig. 5.3e–j (García et al. 2012; Hosono et al. 2010; Li et al. 2010; Shi et al. 2012a, b; Sun et al. 2007; Vapaavuori et al. 2011; Yu et al. 2006a; Zhu and Wang 2013). As pioneered and recently summarized by Zhao and Ikeda (2009), azobenene based LCPs bridged the interdisciplinary fields between polymer, liquid crystals and photochemistry.

Side-chain LCPs based on calamitic mesogens have been so far extensively studied, and various synthetic methods like free radical polymerization, ring-opening metathesis polymerization (ROMP), condensation polymerization and polymer analogous reactions were widely used in the preparation of calamitic type LCPs with variant architectures. However, side-chain LCPs based on discotic mesogen units were much less explored, due to the relatively short history of discovery and certain degree of synthetic difficulties (Kumar 2010). Nevertheless, since the first discotic side-chain LCP reported by Kreuder and Ringsdorf (1983), this field has attracted great attention owing to their capability of self-assembling into well-ordered supramolecular structures, together with various mesophases and unique optoelectronic properties. Up to now, discotic LCs have been demonstrated as promising materials in various applications such as one-dimensional conductors, photovoltaic solar cells, anisotropic photoconductors and especially as optical compensation films in practical liquid crystal display (LCD) (Kumar 2006; Laschat et al. 2007; Sergeyev et al. 2007). The most famous industrially successful case was the negative birefringence optical compensation film made from discotic nematic liquid crystals widely used for enlarging view angles in LCD invented by Fuji photo film lab (Kawata 2002).

Figure 5.4 shows several typical discotic mesogens used in discotic side-chain LCPs. Discotic liquid crystals were first discovered by Chandrasekhar et al. in 1977 (Chandrasekhar et al. 1977). They usually contain two motifs: rigid aromatic core

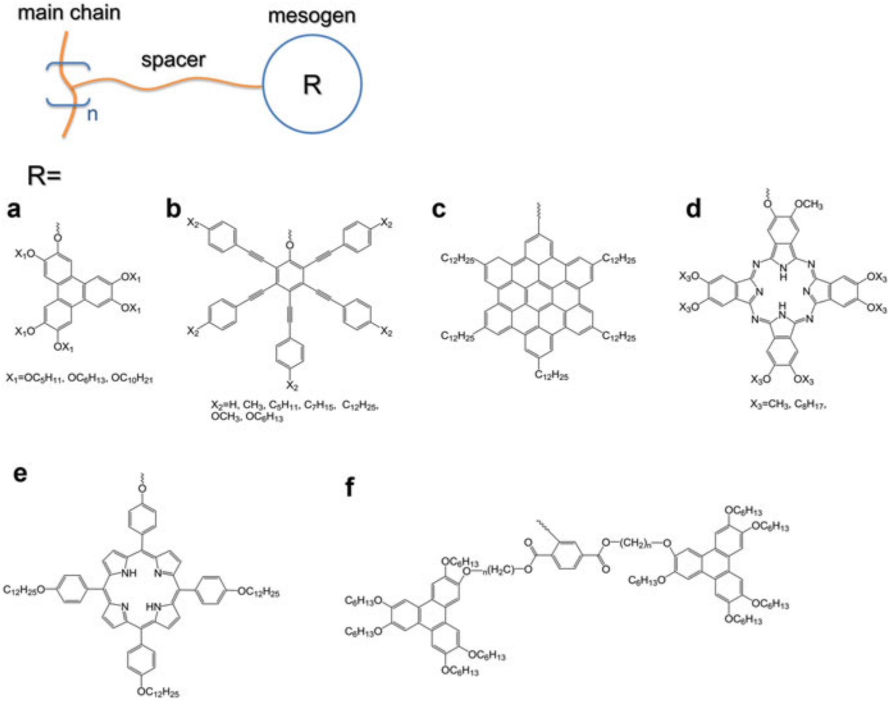

Fig. 5.4 Some typical discotic mesogen units used for side-chain LCPs, and the details of the polymer backbone and spacers are omitted for clarity

with flat or nearly flat structure and several flexible peripheral side chains. Discotic mesogens generally tend to self-organize into columns via π–π stacking, van der Waals' force, and in some cases hydrogen bonding or dipole–dipole interactions (Fletcher and Luckhurst 1995). Other than columnar phases, nematic (Bisoyi and Kumar 2010) and smectic phases (Kouwer and Mehl 2009) can also be formed. Discotic cylinders will further self-assemble into variant 2D columnar mesophases (Fig. 5.5), such as hexagonal columnar phase ($\mathrm{Col_h}$), rectangular columnar phase ($\mathrm{Col_r}$), columnar oblique phase ($\mathrm{Col_{ob}}$), columnar plastic phase ($\mathrm{Col_p}$), columnar helical phase (H) and columnar lamellar phase ($\mathrm{Col_L}$) (Kumar 2006). Taking triphenylene derivatives for example, in ordered columnar phases, the intercolumnar spacing usually ranges from 20 to 40 Å, and the intracolumnar distance (face to face between discs) ranges within 3.5–4.2 Å. The intracolumnar electron conductivity is much larger than intercolumnar conductivity (over 1000 times) (Boden et al. 1993). Such kind of unique columnar assembly feature makes dicotic LC materials promising one-dimensional (1D) conductive organic semiconductors.

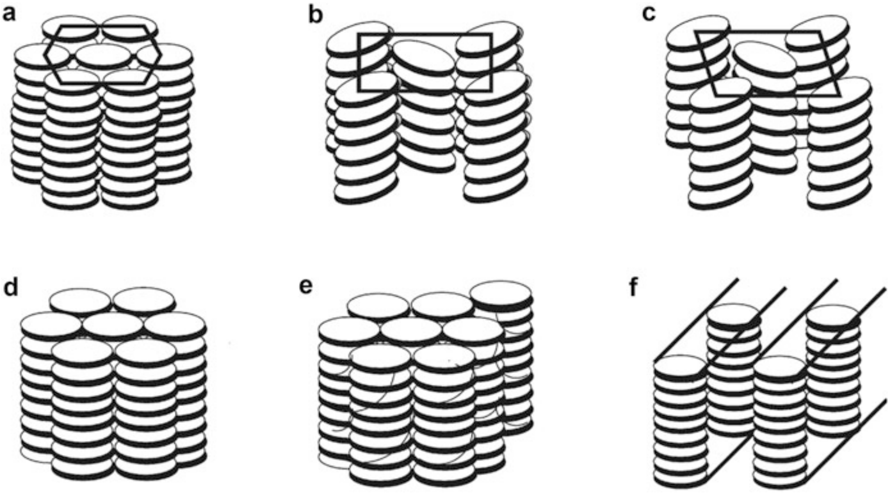

Fig. 5.5 Structures of various columnar phase of discotic meosgens. (**a**) Hexagonal columnar phase (Col_h); (**b**) rectangular columnar phase (Col_r); (**c**) columnar oblique phase (Col_{ob}); (**d**) columnar plastic phase (Col_p); (**e**) columnar helical phase (H); (**f**) columnar lamellar phase (Col_L). Reproduced from {Kumar 2006} with permission of The Royal Society of Chemistry

Many discotic mesogens have been introduced in side-chain LCPs, such as triphenylene (Kreuder and Ringsdorf 1983; Wu et al. 2013) (Fig. 5.4a), alkynylbenzene (Kouwer et al. 2002a, b, 2001, 2003) (Fig. 5.4b), hexabenzocornonene (Thünemann et al. 1999, 2003) (Fig. 5.4c), phthalocyanine (Ganicz et al. 2012; Van der Pol et al. 1989) (Fig. 5.4d) and porphyrin derivatives (de Witte et al. 2003) (Fig. 5.4e). Overall, triphenylene (TP) derivatives are the most widely used discotic mesogens for their relatively easy availability, quite strong self-assembly ability and high performance (Pal et al. 2013). TP core is a kind of rigid planar structure with an 18π aromatic delocalizing electrons, and TP was first proposed as a discotic mesogen by Billard et al. (1978). Most research efforts in TP-based discotic LC materials aim at higher carrier mobility for optoelectronic applications. For instance, hexakis(pentyloxy)triphenylene and hexabutoxytriphenylene render relative high carrier mobility for their highly ordered columnar plastic phases (Adam et al. 1996). Despite that at present the optoelectronic performance of TP-based LCPs is significantly weaker compared with their low molecular weight counterparts, but their suitability for low cost solution process is very attractive and promising for organic electronic material applications such as cheap disposable devices. However, although many polymerization methods have been attempted, so far the road toward preparation of well-controlled TP-based LCPs and optoelectronic high performance is still full of challenges until very recently some essential progress is achieved on their controlled synthesis and hierarchical structure understanding in our lab.

5.3 Synthesis of Side-Chain LCPs: Controlled Radical Polymerization (CRP) and Rational Macromolecular Design

Side-chain LCPs can be readily prepared by direct radical polymerization, ring opening metathesis polymerization (ROMP), ionic polymerization, and step condensation polymerization, etc. Upon considering the polymer backbone and mesogens separately, some specific approaches have also been adopted for side-chain LCP preparation such as polymer analogous reaction and supramolecular assembly.

Condensation polymerization is widely used in construction of main-chain polymers, while its applications in building side-chain LCPs are rare. Some earlier related examples of condensation polymerization were mostly concentrated on combined main-chain and side-chain LCPs (Reck and Ringsdorf 1985). Interested readers are recommended to refer to the Chapter by Zentel in *Handbook of Liquid Crystals* (Demus et al. 1998).

Ring opening metathesis polymerization (ROMP) is a relatively new strategy in polymer synthetic chemistry (Schrock 1990; Bielawski and Grubbs 2007; Trimmel et al. 2005). The key concept of ROMP is based on olefin metathesis which originates from research efforts around mid-1950s. Nowadays, the identification of key intermediates of the olefin metathesis promotes the continuously development of catalysts with definite structure and high efficiency, which in turn significantly boosts broad applications of ROMP, including syntheses of side-chain LCPs with various mesogen units (Weck et al. 1997; Li et al. 2003; Xia et al. 2008; Haque et al. 2013). Due to its living polymerization character, well-defined polymers with predetermined degree of polymerization (DP) and narrow polydispersity index (PDI) can be realized by choosing a suitable catalyst system. Monomers with specific olefin ring structure and complex initiators (or catalysts) system are the main characteristics of ROMP compared with radical polymerization, and moreover, the unsaturated bonds and other functional groups of the monomers will be preserved in the resulting polymers obviously differentiated from products obtained by other methods (Bielawski and Grubbs 2007). These features endow polymers by ROMP with some unique advantages such as sepecial Z/E isomerization and tacticity of the polymer chain. For instance, compared with other living polymerization approaches, ROMP could proceed in air thanks to its wieldy nature and result in much more ordered mesophase structures for SCLCPs (Haque et al. 2013).

Before the broad adoption of controlled radical polymerization methods, controlled cationic polymerization was considered as one of the most successful tools for controlled synthesis of side-chain LCPs for its living polymerization characteristic and suitability for many vinyl ether monomers. An early comprehensive review on this topic was presented by Percec and Tomazos (1992).

Up to now, the overwhelming majority of side-chain LCPs were prepared by conventional radical polymerization, which suffered from high PDI and lack of effective control over molecular weights of the resulting polymers. Although living anionic polymerization is a possible solution, the extremely stringent reaction conditions and limited suitable monomers eventually restrict its broad application in side-chain LCPs. Therefore, nowadays controlled/living radical polymerization (CRP) is becoming more and more widely used in construction of side-chain LCPs with well-controlled molecular weights and narrow PDI, well-defined chain structure and topology under relatively mild reaction conditions. The "living polymerization" concept was first revolutionarily proposed by Szwarc in 1956 based on anionic polymerization (Szwarc et al. 1956). The general principle of controlled/living radical polymerization is to introduce a fast and adjustable equilibrium between active and dormant species, extending the life of propagating chains from milliseconds to minutes or hours thus providing a route to controlled polymerization (Braunecker and Matyjaszewski 2007). So far, several influential CRP techniques have been developed, such as initiator-transfer-termination system (Iniferter), nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT). Regarding the construction of side-chain LCPs, ATRP and RAFT are the most commonly adopted techniques, and we shall therefore mainly focus on these two methods. Interested readers for other two CRP methods can refer to some representative review articles on Iniferter (Otsu and Matsumoto 1998) and NMP (Brinks and Studer 2009).

5.3.1 Side-Chain LCPs Prepared by ATRP Approach

ATRP was discovered almost simultaneously by Matyjaszewski group (Wang and Matyjaszewski 1995) and Sawamoto group (Kato et al. 1995) in 1995. After nearly 20 year's development, the ATRP method becomes simple and easy to operate as well as possessing good reproducibility, especially compatible with various functional groups. A profound review on ATRP was presented by Matyjaszewski and Xia (2001). The functionality of initiators and monomers can be well compatible by ATRP, leading to side-chain LCPs with various functional groups, compositions and topology structures, especially convenient for block copolymers preparation. ATRP initiators with specific functional groups can render the resulting polymers various terminal functionalities. Furthermore, the halogen group capped polymer chain can act as a macroinitiator and continue to initiate other monomers to polymerize thus extending the chain and construct block copolymer or easily realize transformation into other functional groups. These CRP methods are sometimes coupled simultaneously with some high-efficiency postpolymerization reactions such as Click chemistry (Binder and Sachsenhofer 2007; Kolb et al. 2001) and "Post Azo Coupling Reaction" (PACR) (Wang et al. 1997a, b) for the construction of various architectural block copolymers, for instance, star-shaped polymers, grafted polymers and brush-shaped polymers.

Star-shaped side-chain LCPs are usually derived from multi-functional initiators showing particular bulk and solution properties. Zhang et al. (2008) utilized a trifunctional initiator 1,3,5-(2-bromo-2-methylpropionato) benzene for the preparation of three-armed side-chain LCPs via ATRP: a star-shaped MMAZO (methacrylate monomer with azobenzene as side-chain mesogen) based side-chain LC homopolymer PMMAZO or block copolymer PMMAZO-*b*-PMMA. The latter copolymer was obtained using three-arm star PMMA (poly(methyl methacrylate)) as the macroinitiator. Barberá et al. (2008) adopted the same trifunctional initiator for the construction of a similar star-shaped side-chain LCP using an azobenzene mesogen with a chiral center, endowing the polymer with photo-induced chiral arrangements. Recently, He et al. (2009) prepared a star-shaped LCP by ATRP polymerization of MMAZO using a new cyclodextrin (CD) derivative bearing bromide functional groups as the macroinitiator showing potential information memory characteristics.

Liquid crystalling block copolymers (LCBCPs) are usually prepared by adopting macroinitiators as the initial or middle (for ABA or star-shaped copolymers) blocks. End-functionalized PEG/PEO (polyethylene glycol/polyethylene oxide) segments are probably the most widely used macroinitiator, partly because of its good solubility in both water and most organic solvents. As a coil linear polar block, PEG bears high incompatibility with other blocks, offering the driving force for microphase separation. Some well organized review and books by Zhao and Ikeda (2009), Zhao and He (2009) and Wang group (2013) have been published including azobenzene based LCBCPs containing PEG blocks. Very recently, our group (Wu et al. 2013) have just carried out a rational design, controlled synthesis of a series of triphenyene-based discotic LCBCPs via PEG macroinitiators of different lengths, where an intriguing microphase-separated superstructure evolution and columnar order change as a function of temperature and discotic block content have been demonstrated. He et al. (2008) prepared several side-chain ABC triblock LC copolymers by ATRP with different DPs using PEG as the macroinitiator. Wang L et al. (2010) reported a series of side-chain LCPs made of laterally attached photoluminescent *p*-quinquephenyl repeat units using monofunctional PS and PEG as macroinitiators. Some specific macroinitiators for ATRP with more complex structures have been prepared by other polymerization methods such as living cationic polymerization (Gao et al. 2008) and stepwise condensation polymerization (Ishige et al. 2011).

As mentioned above, aside from the macroinitiator pathway, LCBCPs can also be prepared by combining several recently developed high-efficiency reactions like Click chemistry together with ATRP. Click chemistry refers to a highly efficient synthetic strategy that can bind small building blocks together quickly and reliably, usually featuring carbon–hetero atom connections in a mild environment friendly way, which was first proposed by Sharpless (Kolb et al. 2001). The most popular example of Click chemistry is Huisgen's 1,3-dipolar reaction through the Cu^I-catalyzed azide-alkyne cycloaddition (CuAAC). The end halogen groups of the obtained polymers through ATRP provide convenience for transforming into specific groups for subsequent Click procedure, and the functional groups introduced through the initiator well reserved in the resulting polymers can also be used for Click reactions. By means of Click chemistry, various LCBCPs can be prepared conveniently by coupling distinct blocks constructed and characterized separately, which was extremely helpful as a viable route for introducing some specific blocks not available by usual macroinitiator synthetic pathway (Wurm and Frey 2011). It is worthy mentioning that acidic groups are not tolerated by ATRP system, so functional groups like alkynyl hydrogen for Click chemistry should be protected before ATRP process. Recently, Berges et al. (2012) prepared bi-azide-terminated polyesters N_3-PE_x-N_3 by polycondensation and alkyne-functionalized PMMAs via ATRP, then a triblock copolymer was obtained through linking them together via Click reaction. Blasco et al. (2012) “clicked” a LC aliphatic polyester dendron functionalized with sixteen 4-cyanoazobenzene mesogens to a linear block of poly (methyl methacrylate), poly(ethyl methacrylate) or poly(styrene) for the construction of liquid crystalline linear–dendritic block copolymers (LDBCs). Other than Click chemistry, macromolecular azo-coupling reaction was also developed to synthesize LC amphiphilic copolymers together with ATRP. He et al. (2012) carried out such macromolecular azo-coupling reaction between the diazonium salt functionalized PEG and the ATRP-prepared polymer blocks with terminal groups suitable for azo-coupling, leading to a “Y”-shaped LCBCP with an azobenzene group in the middle as a linkage enduing with photoresponsive potential.

Some other applications of ATRP for construction of specific side-chain LCPs such as graft copolymers (Börner et al. 2002; Ferji et al. 2013), cyclic polymers (Laurent and Grayson 2006) and surface initiated polymer (SIP) brushes with LC functionality (Camorani et al. 2009) have also been widely reported.

5.3.2 Side-Chain LCPs Prepared via RAFT Approach

According to Braunecker and Matyjaszewski (2007), there exist two approaches to establish the equilibrium between dormant and active species: persistent radical effect (PRE) as functioning in ATRP method, and degenerative transfer (DT) as operating in RAFT process. RAFT synthesis technique was invented by CSIRO group in Australia (Chiefari et al. 1998), and a French group Charmot at Rhodia Chimie applied a patent with the same mechanism at about the same time (Corpart et al. 1998). Since then, the group of CSIRO continued to work in this fascinating field and presented consecutive reviews on RAFT (Moad et al. 2008, 2009, 2012). Recently, Keddie (2014) reviewed the latest progress of RAFT focusing on the preparation of variant block copolymers. The RAFT polymerization mechanism involves a sequence of addition fragmentation equilibria, and the adoption of a suitable highly efficient chain-transfer agent (CTA) is of crucial importance for a successful RAFT process. CTAs are in principle organic compounds with a thiocarbonylthio moiety that can be briefly described as ZC(=S)SR, wherein double bond C=S is reactive to radical addition and Z substituent endues CTA appropriate reactivity and R substituent serves as a good leaving group capable of efficiently re-initiating polymerization at its radical form R• (Moad et al. 2008; Semsarilar and Sébastien 2010). The reversible chain transfer from a propagating chain to the CTA enables rapid equilibrium between the active propagating radicals and the corresponding dormant species, endowing the polymerization procedure "living" and "controllable" characteristics. RAFT process is generally more similar to traditional radical polymerization, and possesses many advantages compared with other CRP methods like ATRP. A significantly larger range of monomers can be used in RAFT systems. Some monomers like acrylic acid and sodium *p*-styrene sulfonate are not suitable for ATRP method unless with protection of sensitive groups, but they are well tolerated by RAFT systems. Furthermore, from our experience, for side-chain discotic LCPs preparation, ATRP method did not work or could only achieve limited DP while RAFT process operated smoothly in a well controlled way. RAFT approach is also technically metal-free, and easy to process. However, as the key component of RAFT system, the CTAs are not always easy to prepare and the commercial CTAs are usually quite expensive. Although RAFT is a metal-free process, the CTA fragment (thiocarbonylthio group) attached in the resulting polymer will sharpen the final product's toxicity and thus restrict its application in biomedical fields, therefore, on some occasions removal or transformation of the thiocarbonylthio groups become a required procedure (Moad et al. 2008).

RAFT method has been widely and successfully applied in macromolecular engineering of block copolymers (Chong et al. 1999; Convertine et al. 2006; Favier et al. 2004), star-shaped polymers (Huang et al. 2006; Mayadunne et al. 2003; Stenzel and Davis 2002), dendritic polymers (Patton et al. 2008) and surface-initiated polymer brushes (Yu et al. 2004), etc. Applications in building side-chain LCPs have also been widely reported. Hao et al. (2003) prepared a series of side-chain LCPs bearing biphenyl as the mesogen using 2-(2-cyanopropyl) dithiobenzoate (CPDB) as the RAFT agent. The thermal behavior of polymer with different chain lengths was studied, and it turned out that the stable LC mesophase range increased with increasing polymer chain length. Zhao et al. (2008) adopted the same RAFT agent CPDB in preparing the first diblock copolymer with low PDIs composed of two different side-chain liquid crystalline blocks containing azobenzene mesogens. CPDB was also used by Xie et al. (2009) for preparing a novel side-chain LC diblock copolymer PMBHMA-*b*-PMPCS, wherein the PMBHMA (poly[ω-(4$'$-methoxybiphenyl-4-yloxy)hexyl methacrylate]) block was a conventional side-chain LC block, and the PMPCS (poly{2,5-bis[(4-meth-oxyphenyl)oxycarbonyl] styrene}) block was a typical mesogen-jacketed LC block that was capable of assembling into a rigid rod.

The RAFT method offers a convenient pathway to introduce specific blocks into side-chain LCP systems, which renders the polymer functional properties such as amphipathy. Boisse et al. (2009) and Zhang et al. (2012) prepared a series of amphiphilic diblock copolymers via RAFT, wherein the hydrophobic block was a cholesteryl-based smectic LC polymer, while the hydrophilic block was either a neutral polymer with a lower critical solution temperature or a random copolymer with acrylic acid and poly(ethylene oxide) side chains. Zhou et al. (2011) adopted a PEG block as a bifunctional macromolecular RAFT agent (CTA-PEG-CTA) for the construction of novel "LC-semicrystalline-LC" triblock copolymers. Of course, similar to ATRP approach, LC block copolymers can be built by combining specific reactions together with RAFT, such as macromolecular azo-coupling reaction. For example, He et al. (2013) demonstrated an amphiphilic diblock copolymer by a combination of macromolecular azo-coupling reaction and RAFT. Moreover, the organo-catalytic coupling via the thiol-ene Click reaction was adopted for RAFT-prepared precursors in construction of more complex polymer systems such as star-shaped polymers (Chan et al. 2008).

Functionalized CTA itself renders more application possibilities. For instance, Meuer et al. (2008) used α-pyrene containing CTA for preparing α-pyrene functionalized PMMA via RAFT. The polymer itself is not liquid crystalline, but the α-pyrene is an efficient anchoring unit for solubilizing and disentangling multi-walled carbon nanotubes (MWCNTs), which will then self-organize as liquid crystalline phases in PMMA and PEG matrices. However, as mentioned above that the thiocarbonylthio group is detrimental to some applications, so removal or transformation steps are sometimes necessary. In the side-chain LCP films through RAFT method reported by Kawatsuki et al. (2010), the residual dithiobenzoate end groups were thermally decomposed to get colorless polymers. Nevertheless, some modification could be made to utilize the thiocarbonylthio groups as well. Gao et al. (2007) presented a new approach to prepare Ag nanoparticles protected by side-chain LCPs. A homopolymer bearing side-chain azobenzene mesogens was prepared by RAFT, and then the thiocarbonylthio end groups of the obtained polymer were reduced using $NaBH_4$ into thiol groups. The interactions between Ag and thiol groups eventually coated the Ag nanoparticle with side-chain LCPs. Likewise, aside from the thiol group from CTA fragment, another thiol group was introduced at the other end of the polymer chain, and a cyclic polymer with a disulfide linkage was then obtained after a simple oxidation process (Stamenović et al. 2013).

5.3.3 *Other Synthetic Methods for Side-Chain LCPs*

Although most of side-chain LCPs nowadays are obtained by direct radical polymerization, polymer analogous reactions still play an important role in preparing some specific side-chain LCPs. As a matter of fact, the very first discotic side-chain LCP was prepared by attaching discotic mesogens to the polysiloxane main-chain through hydrosilylation reaction (Kreuder and Ringsdorf 1983), which was a typical polymer analogous reaction. Hydrosilylation is a very classical approach in preparing side-chain LCPs that is adopted widely even today. The Si–O bond is highly flexible thus the calamitic side-chain LCPs based on polysiloxane backbone exhibit a strong tendency to form smectic LC phases. Zental group (Beyer et al. 2007; Öge and Zentel 1996) prepared various ferroelectric LC polymers with calamitic mesogens bearing chiral centers attached to polysiloxane backbone via hydrosilylation. Recently, polymer analogous reactions are often combined with CRP methods like ATRP and RAFT. For instance, in a recent work by

Royes et al. (2012), well-defined azobenzene containing side-chain LCPs were achieved through postpolymerization click reactions of azide terminated mesogens with poly(propargyl methacrylate), which was obtained via ATRP with the active alkyne hydrogen of propargyl protected during the ATRP process.

Polymer analogous reaction approach is even more important when the target LCP can not be obtained by direct polymerization from the corresponding mesogenic monomer. For instance, the controlled synthesis of discotic LCBCPs still remains a challenge, and although there were attempts to prepare TP-based homopolymers and block copolymers via ATRP, only limited DP around 8 of the LC block was realized (Otmakhova et al. 2003). Recently, based on block copolymers PEG-*b*-PHEMA via ATRP using PEG macroinitiator, a series of well-defined discotic LC diblock copolymers have been prepared in our laboratory by attaching side-chain triphenylene mesogens to PHEA (poly(2-hydroxyethyl acrylate)) block through polymer analogous esterification (Wu et al. 2013). In general, aminoazobenzene-containing monomers demonstrate significant inhibition effects to free radicals, so the preparation of LCBCPs via CRP with aminoazobenzene or similar push-pull structure mesogens is rather difficult. Wang et al. (2007) prepared a diblock copolymer PEG-*b*-PEMA via ATRP. The PEG block was used as the macroinitiator, and the PEMA block contained side chains with aniline groups. Then the azo-coupling reaction was carried out between the side-chain aniline groups and newly added diazonium salt in a polymer analogous reaction manner, thus a well-defined aminoazobenzene-containing LCBCP was prepared. However, it is worth to note that there always exist difficulties in carrying polymer analogous reaction to 100 % completion, and even high-efficiency reaction and prolonged reaction time can not essentially solve the problem (Wang and Zhou 2004).

Side-chain LCPs obtained via supramolecular self-assembly, on the other hand, demonstrate some interesting specific characteristics compared with the aforementioned approaches. This Chapter will not present detailed comments on such side-chain LCPs and interested readers can refer to critical reviews by Kato et al. (2001, 2006).

5.3.4 Synthetic Approaches for Liquid Crystalline Linear–Dendritic Block Copolymers (LDBCs)

Liquid crystalline block copolymers (LCBCPs) combine the molecular level order of liquid crystals and the nano- or submicrometer scale microphase separation morphology of block copolymers, making them one of the most important research directions in soft matter. Linear–dendritic block copolymers (LDBCs), on the other hand, take a step further from block copolymers by introducing regularly branched and multi-functional dendritic blocks, leading to a promising field for advanced organic nanomaterials. The possible synergistic interactions make LDBCs a promising and inspiring macromolecular platform rather than simple addition of two distinct blocks. Therefore, when mesogenic units are introduced in the dendritic segments of LDBC systems, one can expect even more exciting properties for the liquid crystalline LDBCs such as curvature effect on mesophases and hierarchical superstructure organization.

The idea of LDBCs was first pioneered by Gitsov et al. (1992), and poly(benzyl ether) dendrons of variant generations (called Fréchet-type dendrons) were adopted (Gillies and Fréchet 2002; Gitsov et al. 1993; Gitsov and Frechet 1993; Yu et al. 1999). Based on the pioneering works by Fréchet et al., Percec group carried out systematic and groundbreaking works in developing a family of Percec-type dendrons and their complex self-assembly behavior investigation (Rosen et al. 2009). Critical reviews regarding LDBCs have been presented by Gitsov (2008) and Frey group (Wurm and Frey 2011). Recently, Blasco et al. (2014) reviewed LDBCs bearing stimuli-responsive functional groups, and Dong and Liu (2013) gave a brief review on the applications of LDBCs in bionanotechnology.

As for the synthesis of LDBCs, we would like to give a brief introduction to the preparation methods of dendrimers before going on about LDBCs, considering the importance of dendritic block construction. The synthesis of dendrimers characterizes repeated interactive reactions by multi-branched monomer units, which renders dendrimers precisely controlled structure and large amount of functional terminals. Depending on growing directions, the synthetic routes of dendrimers fall into two basic types: divergent and convergent approaches. The divergent approach was first proposed by Tomalia et al. (1985) and Newkome et al. (1985). In divergent approach, the dendrimer grows from a “core”, followed by the iterative repetition of a two-step synthetic process leading to higher generations. However, the number of active terminals increases dramatically with increasing generation, which may introduce defects due to incomplete reactions. For this reason, products of each procedure have to go through tedious careful purifications. Even so, the divergent approach still remains the most suitable approach for large-scale preparations of many high-generation dendrimers (Wurm and Frey 2011). On the other hand, convergent approach was first adopted by Frechet (1994), wherein dendrimers were prepared via convergent coupling of prefabricated branched units. Nearly all poly(benzyl ether) dendrons were prepared through this route (Wurm and Frey 2011). Limited active sites are involved in each step of convergent approach, which technically reduces the difficulties in reaction completion and for further purification. But for higher generations, the high steric hindrance still evidently depresses the reaction efficiency. Some other less classical synthetic approaches, such as “solid-surface convergent method” (Bharathi et al. 1995) have also been developed.

As for construction of LDBCs, three different strategies are widely used according to the sequence of building linear chain and dendron blocks: the chain-first approach, the dendron-first approach and the coupling approach as schematically presented in Fig. 5.6.

The chain-first approach is in general the most frequently used approach for the preparation of LDBCs, which usually starts from a terminally functionalized linear polymer chain obtained via controlled/living polymerization with the terminal group as the initial point for construction of dendritic part in a divergent manner.

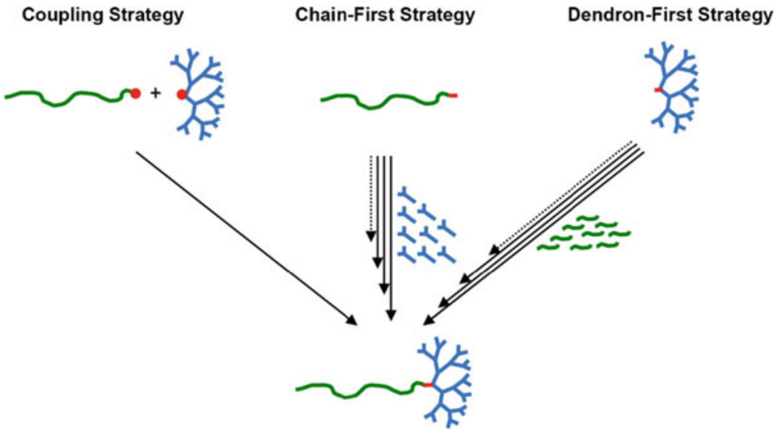

Fig. 5.6 Three strategies for preparing LDBCs. Reprinted from Progress in Polymer Science, 36, Frederik Wurm and Holger Frey, Linear–dendritic block copolymers: The state of the art and exciting perspectives, 1–52, Copyright (2011), with permission from Elsevier

The first example dated back to 1994 by Chapman et al. (1994). The divergent manner of chain-first approach requires 100 % completeness of reactions at each step and entire elimination of the excessive reagents, which is never easy. Still the possibility of some undesired side reactions such as back-folding could introduce defects in LDBCs. The dendron-first approach, on the other hand, requires a dendritic macromolecular initiator, which is mostly prepared through convergent method for preserving an active focal point of the dendron segment. Then, anionic ring-opening polymerization (ROP) and controlled radical polymerizations (CRP) like ATRP, RAFT and NMP were adopted for construction of the linear segment. However, because of the frequently adoption of convergent method in preparing dendrons in dendron-first approach, there still remain some drawbacks as mentioned above from convergent method itself.

The coupling approach achieves the construction of LDBCs through conjugation of the terminal functional group of the linear chain and the active reaction site at focal point of the dendron segment. Actually the coupling approach was exactly the technology adopted in preparing the first LDBC by Gitsov et al. (1992). It turns out that the traditional linear block copolymers are difficult to synthesize in this way due to the strong shielding effects with both coil chains. However, the dendrons usually come with moderate molecular weights and may have some peculiar effects on the coupling efficiency of the focal functionality (Wurm and Frey 2011), which in turn significantly benefit the coupling process. In the first attempt by Gitsov et al. (1992), detailed kinetics study demonstrated that Williamson reaction rate even increased when longer PEG chains and higher generations of the dendron segment were used. Recently, thanks to the intensive development of highly efficient new coupling methods such as Click chemistry, various LDBCs through the coupling approach have been constructed.

5.4 Research Progress of Side-Chain LCPs with Calamitic Azobenzene or Discotic Triphenyene Mesogens: Hierarchical Bulk Structure Evolution, Assembly Behaviors in Solution and Stimuli-Responsive Properties

In this section, we shall present a brief review of side-chain LCPs regarding the structures and properties. Herein, liquid crystalline LDBCs are also included as a specific kind of side-chain LCPs with dendritic side chain LC segments as stated in the previous section. As mentioned in section 2, azobenzene and triphenyene mesogens are typical and the most widely used calamitic and discotic mesogens. Therefore, we shall still focus on LCPs bearing these two types of side-chain mesogens.

5.4.1 Side-Chain LCPs Containing Azobenzene Based Calamitic Mesogens

When talking about macromolecular engineering of azobenzene (AZO) containing side-chain LCPs in the classical way, one may give much consideration on the flexibility/plasticity of the main chain backbone, the length/pliability of the corresponding spacer, the synthesis of mesogen units and the architecture of the whole polymer. Actually, azobenzene containing polymers have gone much further than that, as the photo-isomerization and light-induced motion ability of azobenzene derivatives endue azobenzene based LCPs with fascinating applications.

According to the comprehensive review by Natansohn and Rochon (2002), the motion of azobenzene chromophores within polymers can be classified into three levels: the molecular level, the nanometer scale behavior, and the micrometer (macroscopic) performance. Various optical applications originate from these motion levels, such as photo-induced anisotropy or dichroism (Natansohn and Rochon 2002), photo-induced phase transitions (Zhao and Ikeda 2009), surface relief gratings (SRGs) (Oliveira et al. 2005; Viswanathan et al. 1999), photo-induced chirality (Choi et al. 2007), nonlinear optical (NLO) materials (Yesodha et al. 2004), photomechanics (Ikeda et al. 2007) and command surface (Ichimura 2000). From the critical reviews by Kumar and Neckers (1989), Natansohn and Rochon (1999, 2002), Barrett et al. (2007), Ikeda et al. (2007) and Ichimura (2000), one can cognize the vigorously developed research field.

Other than UV or visible light triggered isomerization, recently, several phenomena of photo-induced motions are becoming the hot topics in the field of side-chain LCPs containing azobenzene. When the polymer film is irradiated with a linear polarized light (LPL), the long axis of AZO mesogens of the polymer will take an orientation almost perpendicular to the polarizing direction, which is widely known as Weigert effect (Yu 2014). Since the *trans*-AZO possesses rigid rod-like geometry while the *cis*-AZO is bent usually resulting in disorder, photo-irradiated phase transition can occur in some cases. Even more, molecular cooperative motion (MCM) (Yu 2014; Zhao and Ikeda 2009), namely the cooperative motions of AZO and photo inert mesogens, endows such kind of LCPs with amplified light responsive properties. Therefore, tailoring of the architecture and content of azobenzene units together with variant backbone topology and spacers renders azobenzene containing side-chain LCPs powerful self-assembling capability and fascinating functions.

There is a close relationship between the photochromic group architecture, phase behavior, thermal properties of bulk polymer, and kinetics of chromophore photoorientation. The constitution characteristics of AZO containing side-chain LCPs make up of the basis for future applications. For instance, the polymer backbone of AZO containing side-chain LCPs may have strong impact on thermal properties, thus significantly influence their mesophases and light-response behavior. Recently, Petr and Hammond (2011) reported a photoresponsive side-chain LCP showing nematic phase at room temperature by attaching AZO mesogens to a polysiloxane backbone. Upon irradiation by UV, the resulting *cis*-form AZO interrupted the nematic order and the bulk film quickly began to undergo isotropization. This phase transition is surprisingly fast, which could be readily observed under POM with black isotropic domains emanating from the nematic Schlieren texture domain boundaries. Similarly, many studies have lately been reported about the effect of several constitution characteristics on the corresponding phase behaviors and light-induced orientations, such as spacers and terminal groups. Recently, several reports performed a series of intensive studies on the effects of alkyl tail length (Chen S et al. 2013), mesogen attaching positions (Yang et al. 2010) and mesogen density (Wang Q et al. 2010) of side-chain AZO containing polymethacrylates. The phase behaviors of polymers were investigated by a combination of multiple characterization techniques such as DSC, POM and SAXS. A series of polymers PMAzoCOOR$_m$ ($m = 1$–18) were prepared with variant alkyl tail length. For $m = 1$–6, the polymers exhibited a SmA phase, while polymers with $m = 2$, 3, 4, and 5 showed an additional SmC phase. For $m = 8$, 10, 14, 18, the polymers exhibited a bilayer SmA phase. Furthermore, polymethacrylates containing *para*-, *meta*- and *ortho*-monosubstituted azobenzene moieties in the side chain were investigated in comparison. The polymers with *para*- and *meta*-monosubstituted azobenzene derivatives exhibited a SmA phase, while those with *ortho*-substituted ones of the most different geometry from traditional “end-on” side-chain LCPs, did not show any LC mesophase at all. LCPs attached by side-chain groups with variant branched single, double, and triple AZO arms were employed for the investigation of mesogen density. Single-armed LCP only exhibited a smetic phase, while double, and triple-armed showed nematic and smetic phases with even broader temperature range. In addition, the clearing temperatures increased with the increasing mesogen densities. Zhu and Wang (2013) prepared similar side-chain LCPs bearing branched AZO side-chain groups with two and three AZO arms, wherein the three-armed AZO polymer showed a well organized SmA mesophase in the lower temperature range. Aside from adding branched arms in a parallel connection style, mesogen density could also be increased in tandem by simply attaching AZOs head to tail. Hosono et al. (2010) prepared a polymer brush carrying three AZO units in series for each side chain. Through a simple one-step hot-pressing process on the oriented Teflon sheet, the polymer achieved large-area 3D order and the resulting polymer film could even behave photomechanical bending without any crosslinking process.

5.4.1.1 Phase Behavior and Superstructure Evolution of Azobenzene Containing Block Copolymers in the Bulk

Block copolymers, which usually demonstrate amphiphilic property by a combination of immiscible blocks, are capable of constructing a variety of ordered nanostructures such as lamellar, cylindrical, double gyroid, and spherical phases through microphase segregation or self-assembly. Liquid crystalline block copolymers (LCBCPs), combining the molecular level order of liquid crystals and the nanometer or sub-micrometer microphase separation structure of block copolymers, constitute a kind of intriguing soft matter materials. A step further, introducing of AZO moieties renders LCBCPs with light-responsive capabilities. The interplay of photo-activity and microphase-separated structure generates exciting possibilities. Abundant reviews have been published in this field (Gohy and Zhao 2013; Yu 2014; Zhao and He 2009). In this section and the next, we shall go over the latest research progress on AZO containing block copolymers in the bulk and in solution.

Considering AZO containing LCBCPs at the bulk solid state, various self-assembled nano-scale domain morphologies can be realized, which can be further readily adjusted by the AZO block LC order and its photoinduced motion. The orientational order of AZO block can be easily tuned by various external stimulations, such as thermal annealing, photo-induced alignment, mechanical orientation and electric/magnetic field (Zhao and Ikeda 2009). Thus the photo-active AZO blocks can trigger optical responsiveness of these block copolymer materials owing to their bringing about motions from molecular level to nanometer scale. On the other hand, the non-LC blocks can also deliver special properties, such as easy solubility, optical transparency (Yu et al. 2007), and photoresponse enhancement (Haque et al. 2012). Komura and Iyoda (2007), Tian et al. (2002), Yu et al. (2006a, b) presented serial impressive works on side-chain AZO containing diblock copolymers. The series of PEG-*b*-PMMAZOs were prepared by ATRP using PEG macroinitiators, wherein PEG blocks of various lengths were adopted as the minority hydrophilic segments and the well-defined AZO containing polymethacrylate PMMAZO blocks were introduced as the hydrophobic, liquid crystalline and photo-responsive majority segments. Periodic nanostructures on the bulk films were developed through the interplay between the microphase separation morphology and the regular periodicity of LC order, as designated as “supramolecular cooperative motions” (SMCMs) (Yu et al. 2006b). Through long-time annealing of the films on the substrate, highly ordered microphase separation with hexagonally arranged PEG cylinders was achieved (Tian et al. 2002). During annealing, the AZO moieties took a perpendicular orientation against the substrate surface, and those PEG cylinders also took a highly ordered perpendicularly orientation through SMCMs. This array-type arrangement and its cross sectional image could be clearly observed using atom force microscopy (AFM) by cleavage preparation (Komura and Iyoda 2007). Different orientation directions of the PEG cylinders could also be readily realized through rubbing (Yu et al. 2006b) or photo-induced alignment (Yu et al. 2006a). Morikawa et al. (2007) prepared a similar diblock copolymer using PS as the non-LC segment instead of PEG. Microphase separated nanocylinder domains of PS were introduced by a combination of LPL irradiation and annealing followed by slow cooling process. For real-time monitoring of the corresponding microphase separation and photo-orientation procedure by LPL, a poly(butyl methacrylate) (PBMA) block was introduced in replacement of PS block by the same group (Fukuhara et al. 2013; Nagano et al. 2012). The resulted PBMA-*b*-PMMAZO copolymers were then examined with time-resolved SAXS/WAXS and GI-SAXS.

A family of “ABA-type” triblock copolymers were prepared by He et al. (2003), Tang et al. (2007a, b) and Kadota et al. (2005), wherein a central PEG block (macroinitiator) were sandwiched by two terminal PMMA blocks containing side-chain AZO units. Crystalline, smetic and/or nematic phases were observed for triblock copolymers of different compositions. The DSC study indicated that PEG crystallization only occurred above weight fraction 42 %, otherwise due to interfaces enhancement between the PEG and LC blocks with increasing AZO block content, crystallization of PEG block was eventually completely suppressed (He et al. 2003; Tang et al. 2007a). The tail substituent effects of AZO mesogens were also investigated (Tang et al. 2007b). Through Langmuir-Blogett technology from water surface, clear AFM images of this ABA triblock copolymer monolayer on mica were observed (Kadota et al. 2005). The monolayer with their AZO units in *cis*-form gave characteristic elongated branched flat stripe patterns with about 30 nm widths in topological AFM images. After thermal reversion to the *trans*-form, the stripe-shaped domains turned into dot structures. The difference in compatibility with water between *cis*-AZO and *trans*-AZO contributed to this organized morphology difference of AFM images.

Recently, Menghetti et al. (2012) carried out a comparative study regarding optical writing properties between block copolymer and random copolymer based on azobenzene methacrylate (MAZO) LC monomer and methyl methacrylate (MMA) co-monomer. It turned out that stable and intense pulses as short as 100 ms could develop a significant local birefringence increase for the block copolymers thanks to their microphase separation, whereas not for the corresponding random copolymer. Chen et al. (2011) reported a detailed study on the phase diagram of polystyrene-*b*-poly(n-butyl methacrylate) (PS-*b*-PnBMA) block copolymers, wherein AZO units were attached to the PnBMA block through postfunctionalization replacing the butyl side group at different degree, thus the content of AZO units could be adjusted. LCBCPs with similar structure feature were prepared by Del Barrio et al. (2013) attaching the AZO units to the poly (4-vinylpiridine) block via supramolecular self-assembly approach. Han et al. (2010) synthesized the first example of diblock copolymer containing both poly(3-hexylthiophene) (P3HT) and side-chain AZO block. The AZO block was designed with a higher clearing temperature than P3HT block, in which way the AZO block showed liquid crystalline property while keeping the P3HT block in its isotropic phase. Then the alignment of the P3HT nanodomains could be well adjusted along with the photo-induced orientation of AZO units.

Besides linear LCBCPs, the bulk and solution behaviors of linear-dendritic block copolymers (LDBCs) have also been extensively studied. However, so far very few studies appeared on LDBCs with mesogens showing liquid crystalline mesophases, despite this kind of novel LCBCPs has been predicted more than a decade ago (Demus et al. 1998). Recently, a series of azobenzene containing LDBCs were synthesized, and systematic investigations were carried out on their bulk (Blasco et al. 2012; Del Barrio et al. 2009), solution (Blasco et al. 2013a, b; Del Barrio et al. 2010) and LB film (Giner et al. 2011) behaviors. Theoretical simulation studies on these AZO containing LDBCs were also reported by Lin et al. (2012) lately. Most of the reported AZO containing LDBCs were composed of a linear PEG segment and an AZO containing dendritic aliphatic ester block PDMPA of different generations from 2,2-bis(hydroxymethyl)propionic acid (bis-MPA). The self-organization behaviors of these LDBCs in solution, which will be discussed in the next section, were extraordinary rich, while the bulk morphology was quite monotonous with largely lamellar structures as revealed by XRD and TEM investigations, even when the linear PEG segment was replaced by other different blocks such as PMMA, poly(ethyl methacrylate) (PEMA) or PS (Blasco et al. 2012).

Nevertheless, multiple mesophases and hierarchical superstructures in the bulk solid-state can be achieved by rational design of the AZO containing dendritic segments. Recently, our group (Shi et al. 2012a, b) synthesized a series of LDBCs consisting of a linear PEG block (DP = 49) and dendritic polyamidoamine (PAMAM) segments of generation G0–G3, wherein AZO units bearing an octyloxy tail and a flexible ten-methylene spacer were attached at the periphery of the PAMAM dendron (Fig. 5.7). Their thermal behaviors, liquid crystalline mesophases and hierarchical superstructures were intensively studied by a combination of TGA, DSC, POM, SAXS/WAXS and TEM. Along with increasing generations, a hierarchical structure evolution exhibited. LDBCs composing dendrons of G0–G2 demonstrated well-defined lamellar structures, where distinct microphase separation between the hydrophilic PEG blocks and hydrophobic PAMAM dendrons occurred, with only a slight change in layer spacing between 12.2 and 13.0 nm. Among them, mPEG-G0-$(AZO)_2$ displayed a simple lamellar structure (Fig. 5.7b), while owing to further microphase separation between PAMAM dendrons and AZO units within the dendritic blocks, mPEG-G1-$(AZO)_4$ and mPEG-G2-$(AZO)_8$ developed into hierarchical structures of "tetragonal-within-lamellar" (Fig. 5.7c) and "lamellar-within-lamellar" (Fig. 5.7d),

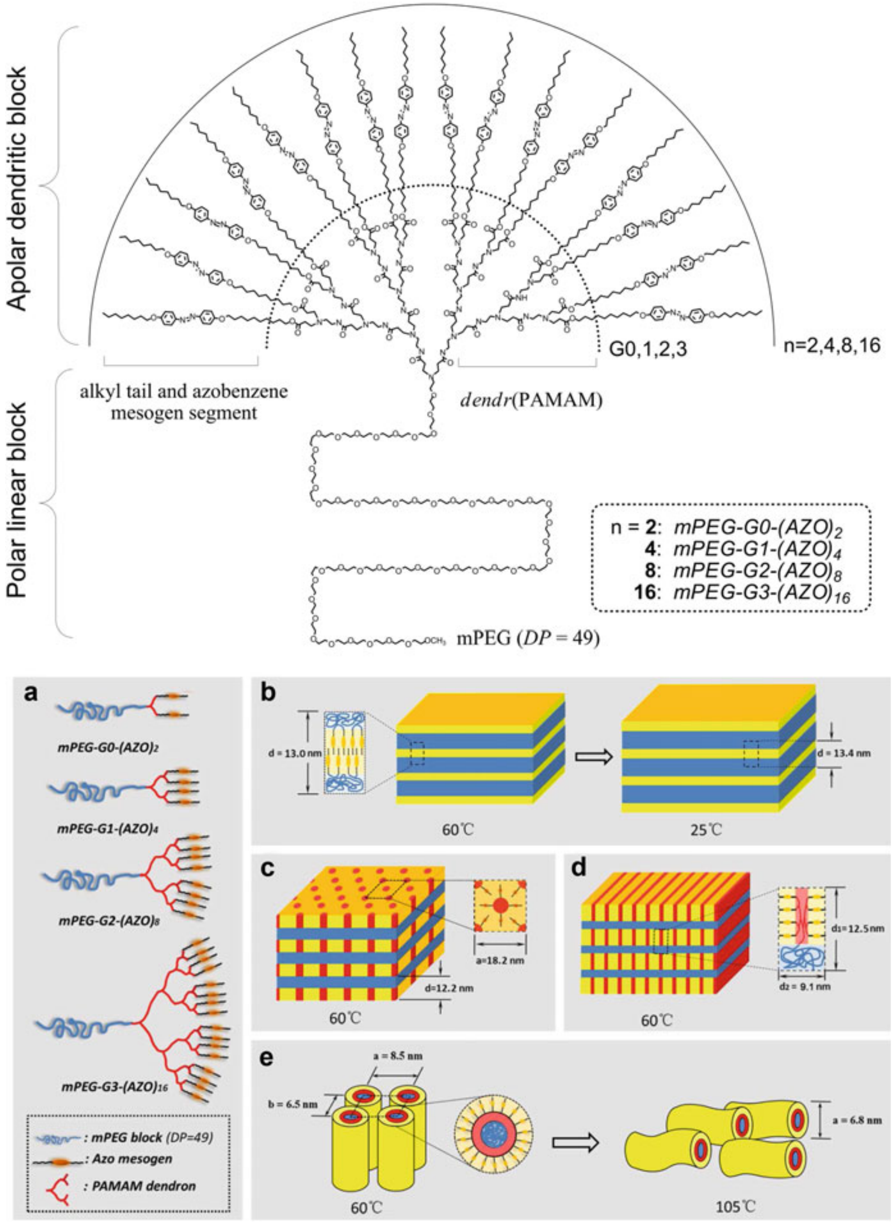

Fig. 5.7 Molecular structures of a series of AZO containing LDBCs with a PEG linear block and PAMAM dendritic segments and proposed model for self-assembled superstructures of various generation LDBCs and their liquid crystalline mesophases. Reproduced from (Shi et al. 2012b) with permission of The Royal Society of Chemistry

respectively. Different from aforementioned generally lamellar structure with some intralamellar structure suborganization, a striking real columnar structure was formed for LDBC with the investigated highest generation mPEG-G3-$(AZO)_{16}$. These columns organized in 2D rectangular structure at low-temperature with the PEG core and the peripheral AZO mesogens, while disaggregated into a disordered columnar mesophase upon heating to higher temperature. In this study, the adoption of alkyloxy tails for the AZO units is crucial for the construction of hierarchical superstructures and mesophases, for similar LDBC systems with nitroazobenzene groups attached through six-methylene spacer examined in our laboratory even did not show a distinct phase separation structure. Moreover, it turned out that the complex lamellar mesophases of G1 and G2 LDBCs transformed into micellar or network cubic structures upon cooling to ambient solidification temperature with PEG crystallization, which demonstrated a complete inverse phase change tendency due to the curvature effect of the specific linear–dendritic architecture. Furthermore, such kind of azobenzene-containing liquid crystalline LDBCs films displayed generation dependent or morphology determined photophysical characteristics, therefore, novel optical storage materials might be designed and fine-tuned just by simply changing the dendritic segment generation.

5.4.1.2 Assembled Structures of Azobenzene Containing Block Copolymers in Solution

Amphiphilic property can be easily introduced into LCBCPs by specific macromolecular engineering. By rational macromolecular design and proper solvent combination choice, various self-assembled aggregates such as vesicles and micelles or more complicated structures, can be realized in solution of LCBCPs, leading to many specific properties and applications (Discher and Eisenberg 2002; Li and Keller 2009; Rosler et al. 2001). Adoption of AZO units in amphiphilic LCBCPs assembly renders the system photo-responsive characteristics. For instance, LPL-induced orientation (Weigert effect) of AZO units brings about photo-induced assembly deformations, and the AZO *trans–cis* isomerization can result in micelle disaggregation or vesicle fusion. Wang group (Li et al. 2005, 2006; Liu et al. 2008, 2009, 2010) performed systematical investigation on photo-induced deformation of colloidal spheres based on amphiphilic AZO polymers. The LCP colloidal spheres elongated along the polarization direction of the incident Ar^+ laser, and the effects of several structural factors on the deformation were detailedly discussed. Su et al. (2007) reported the real-time fusion process of the giant micro-vesicles under the irradiation of 365 nm light based on amphiphilic AZO containing LCBCPs.

Spherical micelles are the most commonly obtained assemblage in solution from AZO containing LCBCPs. The AZO blocks usually show hydrophobic character and form the micelle core, while the other hydrophilic segments like PEG shape the corona. Thus, through the response of AZO units, photo-induced morphological change of micelles can be realized. Recently, Jochum and Theato (2010) reported a temperature and light controlled micelle formation and disruption. Solution of the block copolymer poly(ethyleneoxide)-*b*-poly(*N*-isopropylacrylamide) (PEO-*b*-PNIPAM), wherein azobenzene units was adopted as side groups in PNIPAM blocks, demonstrated micelle formation when heated from 20 to 50 °C and the process was fully reversible, which was confirmed by turbidimetry, fluorescence, NMR and dynamic light scattering (DLS) measurements. Also, micellar disruption was observed by UV irradiation and the micelle reformed after a thermal relaxation process. Besides micellar disruption by *trans–cis* isomerization, it was demonstrated that in another research of AZO containing LCBCPs, where non-radiative *trans–cis* isomerization relaxation of azobenzene moiety was hindered, UV irradiation could also influence the intensity of fluorescence emission through the formation and size change of aggregates (Xiang et al. 2010). Recent years, the reversible host-guest inclusion complexation between AZO and cyclodextrin (CD) has been widely investigated in polymer systems (Tomatsu et al. 2005; Yan Q et al. 2011). Through hydrophobic and van der Waals interactions, *trans*-AZO matches well with CD thus forming inclusion complex, while *cis*-AZO does not. Thus, AZO containing block copolymers can self-assemble into micelles through host-guest complexation between β-CD and *trans*-AZO side groups, whereas transformation into *cis*-AZO will result in disassembly. In a recent example presented by Wang et al. (2013), micelles formed in aqueous solution from PAZO-*b*-PS diblock copolymer and β-CD demonstrated reversible disassembly and re-assembly with alternating UV and visible light irradiation.

Preparation of vesicles from AZO containing LCBCPs was also extensively studied. Similarly, features of the resulting vesicles such as size, regularity, fluorescence emission and morphology can also be tuned via AZO units through light irradiation. Recently, Dong et al. (2013) reported a reversible fluorescence decrease and recovery phenomenon during the *trans–cis* isomerization process of the vesicle formed from poly(ethylene glycol)-*b*-poly(dimethylamino azobenzene) (PEG-*b*-PDMA-AZO) in solution. Yan B et al. (2011) reported a photo-softening effect on the proton transfer across the vesicle membrane. Other photo-induced effects such as UV/visible light induced vesicle fission (Chen K et al. 2013) and LPL induced vesicle deformation (Wu et al. 2011) were also reported from AZO containing LCBCPs. Besides, sizes and morphologies of vesicles can usually be adjusted via rational molecular design of AZO containing amphiphilic LCBCPs. Structural factors such as content of AZO units (Jin et al. 2010) and the corresponding spacer lengths (Shen et al. 2013) have demonstrated significant effects on the shape and morphologies of vesicles.

For AZO containing linear–dendritic block copolymers (LDBCs), even more abundant self-assembly structures have been observed from solutions. As mentioned in Sect. 5.4.1.1, Blasco et al. (2013a, b), Del Barrio et al. (2010) presented systematic investigations on the solution behaviors of such kind of LDBCs. Solution behavior (Shi et al. 2012a) of a series of liquid crystalline LDBCs was also carried out in our lab with azobenzene mesogens as mentioned in the previous section: mPEG-*dendr*(PAMAM)-(AZO)$_n$($n = 2, 4, 8, 16$), wherein the effect of water content in the dioxane/H_2O mixed solution and initial copolymer concentration were investigated especially for the lower generation dendritic segment copolymers. G0 copolymer mPEG-*dendr*(PAMAM)-$(AZO)_2$ assembled into nanofibers in a solution with 28 wt% water, and nanospheres were formed when water content increased. G1 copolymer mPEG-*dendr*(PAMAM)-$(AZO)_4$ formed nanospheres in a solution with 17 wt% water, and oval sheets were obtained with nanorods attached to both ends when water content reaching 28 wt%. Such peculiar oval sheet assemblies, which might represent the intermediate state between one-dimensional nanofibers and two-dimensional nanosheets, were reminiscent of the formation of membranes in biosystems, and could possibly open a new pathway for construction of biomimetic structures. Moreover, polymeric vesicles and large compound micelles (LCMs) were generated from G2 and G3 copolymers in solution respectively.

5.4.2 Phase Behavior and Hierarchical Structures of Polymers Containing Triphenylene Based Discotic Mesogen Side Groups

The first reported discotic LC polymer was a polysiloxane bearing triphenylene (TP) based discotic mesogens as the side chains via hydrosilylation reaction (Kreuder and Ringsdorf 1983). Several critical reviews and books on polymers containing TP mesogenic units have been presented (Bisoyi and Kumar 2010; Kumar 2004, 2005). The spacer effect was preliminarily investigated by Werth and Spiess (1993) mainly based on TP-based polysiloxane backbone side-chain LCPs. It was found that in contrast with the calamitic LC polymer system where the decoupling of the mesogen from the polymer main chain was of crucial importance and became more effective with increasing spacer length, for discotic LC polymers, the longer spacers did not lead to higher ordered phases, presumably due to the decoupling aspect of the spacer was overruled by the diluting perturbation on the columnar packing, and the columnar phases reacted by a change in symmetry or by a distortion of the resulting mesophases even resulted in the breakdown of the columnar phase.

Polysiloxane is a kind of very flexible polymer backbone, thus the adoption of more universal backbones like polymethacrylate or polyacrylate is quite desirable for side-chain discotic LCPs. However, only nematic columnar (N_{col}) phases complexed with trinitrofluorenone (TNF) through charge-transfer (CT) interactions were observed from the early attempts by Ringsdorf et al. (1989). Generally, the rigid polymethacrylate backbone suppressed the formation of LC mesophases, unless properly modified with flexible diethylenoxy spacer (Boden et al. 1998). Talroze et al. (2000) prepared random copolymers based on the monomers of TP-containing methacrylate and hydroxyethyl acrylate, which showed wide range columnar mesophases.

More diverse backbones were introduced with some specific polymerization techniques, such as step condensation polymerization (Catry et al. 1993; Imrie et al. 2004; Karthaus et al. 1992; Ringsdorf et al. 1989) and ROMP (Weck et al. 1997). For instance, Karthaus et al. (1992) reported a combined main-chain and side-chain LC polymers via condensation polymerization, wherein both AZO and TP units were introduced, while the resulting polymers did not show any LC mesophases. Weck et al. (1997) synthesized discotic LCPs bearing alkoxy-substituted TP moieties in the side-chain by ROMP using ruthenium catalysts. The original backbones were poly(norbornene) or poly(butadiene), and hydrogenation of the poly(butadiene) using Crabtree's catalyst gave saturated poly(butane)-backbone polymers. It turned out that discotic hexagonal columnar mesophases were realized only for decyloxy-substituted TP-based polymers while not for the pentoxy-substituted TP systems.

Xing et al. (2008) synthesized rigid poly(1-alkyne) carrying side-chain TP units with different peripheral alkyloxy chain lengths. The polymers with shorter and longer peripheral alkyloxy chains adopted a hexagonal columnar structure, while those intermediate ones formed mixed mesophases. Recently, the same group reported a new type of liquid crystalline polyacetylene containing side-chain TP units with very short spacers (Yu et al. 2013), which exhibited mesogen jacketed liquid crystalline polymer (MJLCP) properties. Side-chain TP-containing MJLCPs with different spacer lengths (n) between the central paraphthalate and TP units were also reported (Zhu et al. 2012, 2014). In this case, the T_g of resulting polymers decreased with longer spacers. Polymers with relatively short ($n = 3$) or medium spacers ($n = 6$) demonstrated rectangular or hexagonal columnar mesophases at higher temperature and merely rectangular columnar mesophase at lower temperature, wherein the TP units formed discotic nematic (N_D) phase within the columns. As for the longest spacer ($n = 12$), the low-temperature phase was a hexagonal columnar structure, and the high-temperature phase was an N_{col} phase formed by the MJLCP chain as a whole. Specially, a re-entrant isotropic phase was found in the medium temperature range.

Side-chain TP units were also introduced in some specific polymer systems. Pal and Kumar (2008) prepared a novel ionic discotic liquid crystalline polymer from TP-substituted 1-vinylimidazole monomer for combining ionic liquids and discotic liquid crystals. A transition from glassy state to rectangular columnar phase of the polymer took place at 224 °C and the columnar LC phase sustained till 244 °C. Recently, Tahar-Djebbar et al. (2011) and Zeng et al. (2014) reported a series of π-conjugated polythiophene bearing TP units in the side chains. Novel hierarchical "lamello-columnar" phases were developed, wherein the TP units constituted a 2D columnar lattice and the main-chain formed the general lamellar structure.

Although new advances keep emerging from various very closely related fields since the introduction of TP into polymeric systems, whereas the precise synthesis of homopolymers and block copolymers containing side-chain TP units with well-defined structures and compositions remains a challenge. In an early attempt by Boden et al. (1999), TP-containing LCBCP was obtained by attaching TP units to poly(p-methoxystyrene)-*b*-poly(p-hydroxystyrene) backbone via polymer analogous reaction, while the resulting block copolymer did not show any LC mesophases. Likewise, through polymer analogous reactions, Stillings et al. (2010) prepared TP-based side-chain homopolymer and block copolymer by attaching TP units to poly(but-3-en-1-ol) and poly(but-3-en-1-ol)-*b*-polystyrene backbones. It is interesting to find that in the bulk films of the block copolymer, microphase separation took place between the TP-containing poly(but-3-en-1-ol) block and the PS block leading to a ordered smetic phase, wherein the TP units assembled into cylinders lying perpendicularly to the microphase separated layers, which demonstrated a uniform perpendicular TP columnar orientation induced by "slit-like" nanospace confinement.

Despite polymer analogous reactions have been widely employed with some relatively successful examples, their intrinsical shortage of incomplete reaction makes them unsuitable for the preparation of strictly well-defined polymers. Thus many efforts have been making to synthesize TP-containing LC polymers through direct synthesis such as radical polymerization. Otmakhova et al. (2003) reported TP-based side-chain block copolymers of 2,6,7,10,11-pentapentyloxy-3-(3-acryloylpropyloxy) triphenylene (PPAT) and *tert*-butyl acrylate (*t*-BA) through ATRP. This approach eventually obtained the homopolymer with a limited DP around 8, which might originate from the special assembly of monomers in solution. Nevertheless, the resulting homopolymer could be used as the macroinitiator for variant molecular weight block copolymer preparation through polymerization of *t*-BA by ATRP. All the resulted LCBCPs with different poly(*t*-BA) block contents displayed microphase separation, and XRD measurements confirmed that both the homopolymer and block copolymers showed columnar mesophases.

Very recently, our group (Wu et al. 2013) synthesized a well-defined block copolymer poly(ethylene glycol)-*b*-poly(2-hydroxyethyl acrylate) (PEG-*b*-PHEA) with PEG macroinitiators of various molecular weights via ATRP, then a series of side-chain discotic LCPs were prepared by attaching side-chain triphenyene mesogens to the PHEA block through polymer analogous esterification (Fig. 5.8). The resulting block copolymers, with various discotic LC block weight fraction ($f_{\mathrm{w,DLC}}$), showed a narrow PDI value no larger than 1.11. Thermal behaviors and corresponding mesophase structures as a function of $f_{\mathrm{w,DLC}}$ and temperature were studied by a combination of POM, DSC and SAXS/WAXS. At relatively low temperatures, block copolymers with lower DLC contents ($f_{\mathrm{w,DLC}} = 37$ and 43 %) formed lamellar structures and underwent order-order transitions (OOT) upon PEG region crystallization at 45 °C, meanwhile a phase transition from $\mathrm{N_D}$ to $\mathrm{N_{col}}$ took place at about 25 °C within the microdomain of TP units. In case of intermediate $f_{\mathrm{w,DLC}}$ value (62 %), hexagonal packed cylinders (HPCs) of amorphous PEG segments were formed above 35 °C within the matrix of TP moieties, which eventually turned into a mixed lamellar structure upon cooling below 35 °C together with PEG crystallization. HPC structures were also generated in copolymers with higher $f_{\mathrm{w,DLC}}$ (67 and 80 %), in which case the TP matrix showed $\mathrm{N_D}$ or $\mathrm{N_{col}}$ mesophases. In the case of the highest $f_{\mathrm{w,DLC}}$ (around 90 %), an overall $\mathrm{N_D}$ phase was developed. The compared homopolymer prepared from small molecular

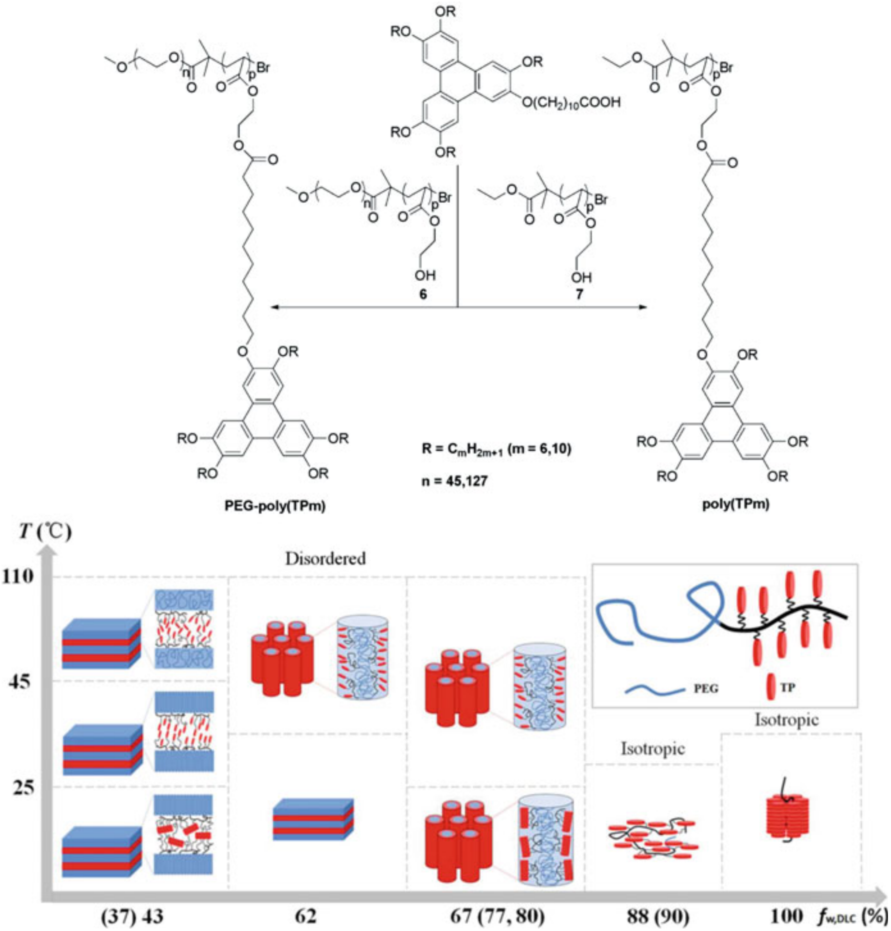

Fig. 5.8 Chemical structure of the block copolymers and schematic presentation of the hierarchical superstructure evolution. Reprinted with permission from (Wu B, Mu B, Wang S, Duan J, Fang J, Cheng R, Chen D (2013) Triphenylene-based side chain liquid crystalline block copolymers containing a PEG block: controlled synthesis, microphase structures evolution and their interplay with discotic mesogenic orders. Macromolecules 46: 2916–2929). Copyright (2013) American Chemical Society

initiator, on the other hand, demonstrated an ordered columnar phase. The presence of an overall N_D phase in the high discotic LC content copolymer is quite inspiring, for it may open a new way for achieving such important discotic LC mesophase applying in widening view angle for liquid crystal display (LCD) just by introducing an appropriate short block. This study enhanced the understanding of the interplay between microphase separation and discotic LC order, which would inspire further explorations for side-chain discotic LCPs leading to various applications.

5.5 Conclusions and Future Perspective

In this Chapter, we have reviewed the recent research progress in the side-chain liquid crystalline polymers (LCPs) mainly based on typical rod-like (calamitic) mesogen azobenzene derivatives and disc-like (discotic) mesogen triphenylene (TP) derivatives. Three main aspects have been focused on: controlled synthesis, rational macromolecular design and LC mesophase behaviors pertaining to their hierarchical structures. Controlled syntheses via CRP methods especially ATRP and RAFT endue the resulted polymers many attributes such as well-controlled DP and narrow PDI, well-defined architecture and terminal groups under relatively mild reaction conditions. With such advantages ATRP and RAFT synthesis techniques have made tremendous contributions to macromolecular design of side-chain LCPs. Rational consideration should be given to the backbone, the spacer, the mesogen units and many other factors regarding the construction of side-chain LCPs. Among mesogenic units, calamitic azobenzene derivatives possess rigid skeletons as well as fascinating photo-responsive properties, and discotic triphenylene derivatives are widely used for their easy availability, powerful self-assembly ability and high performance. In complex side-chain LCP systems, the coexistence and interplay of hierarchical superstructures and LC mesophases may lead to various novel intriguing applications.

Particularly, liquid crystalline block copolymers (LCBCPs) give a chance for investigating the LC phase behavior within constrained nanodomains as a consequence of microphase separation of distinct blocks. On the other hand, the morphological nanodomains of block copolymers will be modified and adjusted by mesogenic ordering and orientation. As a hot research field in soft matter materials, LCBCPs combining molecular level LC order and nano- or submicrometer scale microphase separation morphology may serve as intriguing advanced organic optoelectronic materials. They can also be employed as fascinating templates for controlled preparation of inorganic semiconductors or hybrid functional materials.

References

Adam D, Roemhildt W, Haarer D (1996) Charge-carrier transport in liquid-crystal based organic photoconductors. Jpn J Appl Phys 1(35):1826–1831

Akiyama E, Nagase Y, Koide N, Araki K (1999) New side chain liquid crystalline polymers: synthesis and thermal properties of side chain polyacrylates having segmented spacers. Liq Cryst 26:1029–1037

Barberá J, Giorgini L, Paris F, Salatelli E, Tejedor RM, Angiolini L (2008) Supramolecular chirality and reversible chiroptical switching in new chiral liquid-crystal azopolymers. Chemistry 14:11209–11221

Barrett CJ, Mamiya J, Yager KG, Ikeda T (2007) Photomechanical effects in azobenzene-containing soft materials. Soft Matter 3:1249–1261

Berges C, Javakhishvili I, Hvilsted S, Sánchez C, Alcalá R (2012) Photoresponsive azopolyester-PMMA block copolymers obtained by combination of ATRP, polycondensation, and “click” chemistry. Macromol Chem Phys 213:2299–2310

Beyer P, Krueger M, Giesselmann F, Zentel R (2007) Photoresponsive ferroelectric liquid-crystalline polymers. Adv Funct Mater 17:109–114

Bharathi P, Patel U, Kawaguchi T, Pesak DJ, Moore JS (1995) Improvements in the synthesis of phenylacetylene monodendrons including a solid-phase convergent method. Macromolecules 28:5955–5963

Bielawski CW, Grubbs RH (2007) Living ring-opening metathesis polymerization. Prog Polym Sci 32:1–29

Billard J, Dubois JC, Huutinh N, Zann A (1978) Mesophase of disc-like molecules. Nouv J Chim 2:535–540

Binder WH, Sachsenhofer R (2007) ‘click’ chemistry in polymer and materials science. Macromol Rapid Commun 28:15–54

Bisoyi HK, Kumar S (2010) Discotic nematic liquid crystals: science and technology. Chem Soc Rev 39:264–285

Blasco E, Barrio JD, Piñol M, Oriol L, Berges C, Sánchez C, Alcalá R (2012) Azobenzene-containing linear–dendritic block copolymers prepared by sequential ATRP and click chemistry. Polymer 53:4604–4613

Blasco E, Serrano JL, Piñol M, Oriol L (2013a) Light responsive vesicles based on linear-dendritic block copolymers using azobenzene-aliphatic codendrons. Macromolecules 46:5951–5960

Blasco E, Del Barrio J, Sánchez-Somolinos C, Piñol M, Oriol L (2013b) Light induced molecular release from vesicles based on amphiphilic linear-dendritic block copolymers. Polym Chem 4:2246–2254

Blasco E, Piñol M, Oriol L (2014) Responsive linear-dendritic block copolymers. Macromol Rapid Commun 35:1090–1115

Boden N, Bushby RJ, Clements J (1993) Mechanism of quasi-one-dimensional electronic conductivity in discotic liquid crystals. J Chem Phys 98:5920–5931

Boden N, Bushby RJ, Lu ZB (1998) A rational synthesis of polyacrylates with discogenic side groups. Liq Cryst 25:47–58

Boden N, Bushby RJ, Lu Z, Eichhorn H (1999) Discotic liquid crystalline block copolymers 1: side-chain discotic liquid crystalline diblock copolymers. Mol Cryst Liq Cryst Sci Technol A 332:2791–2801

Boisse S, Rieger J, Di-Cicco A, Albouy P, Bui C, Li M, Charleux B (2009) Synthesis via RAFT of amphiphilic block copolymers with liquid-crystalline hydrophobic block and their self-assembly in water. Macromolecules 42:8688–8696

Börner HG, Duran D, Matyjaszewski K, Da Silva M, Sheiko SS (2002) Synthesis of molecular brushes with gradient in grafting density by atom transfer polymerization. Macromolecules 35:3387–3394

Braunecker WA, Matyjaszewski K (2007) Controlled/living radical polymerization: features, developments, and perspectives. Prog Polym Sci 32:93–146

Brinks MK, Studer A (2009) Polymer brushes by nitroxide-mediated polymerization. Macromol Rapid Commun 30:1043–1057

Camorani P, Cristofolini L, Fontana MP, Angiolini L, Giorgini L, Paris F (2009) Azo-containing polymer brushes: photoalignment and application as command surfaces. Mol Cryst Liq Cryst 502:56–64

Catry C, Van der Auweraer M, De Schryver FC, Bengs H, Häussling L, Karthaus O, Ringsdorf H (1993) Conductivity and photoconductivity of undoped and doped Langmuir-blodgett films of a polymer with hexaalkoxytriphenylene side-groups. Die Makromol Chem 194:2985–2999

Chan JW, Yu B, Hoyle CE, Lowe AB (2008) Convergent synthesis of 3-arm star polymers from RAFT-prepared poly (n, n-diethylacrylamide) via a thiol-ene click reaction. Chem Commun 40:4959–4961

Chandrasekhar S, Sadashiva BK, Suresh KA (1977) Liquid crystals of disc-like molecules. Pramana 9:471–480

Chapman TM, Hillyer GL, Mahan EJ, Shaffer KA (1994) Hydraamphiphiles: novel linear dendritic block copolymer surfactants. J Am Chem Soc 116:11195–11196

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

Chen W, Wei X, Balazs AC, Matyjaszewski K, Russell TP (2011) Phase behavior and photoresponse of azobenzene-containing polystyrene-block-poly (n-butyl methacrylate) block copolymers. Macromolecules 44:1125–1131

Chen K, Xue G, Shen G, Cai J, Zou G, Li Y, Zhang Q (2013) UV and visible light induced fission of azobenzene-containing polymer vesicles. RSC Adv 3:8208–8210

Chen S, Ling A, Zhang HL (2013) Synthesis and phase behaviors of side-chain liquid-crystalline polymers containing azobenzene mesogen with the different length alkyl tail. J Polym Sci A Polym Chem 51:2759–2768

Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TP, Mayadunne RT, Meijs GF, Moad CL, Moad G, Rizzardo E, Thang SH (1998) Living free-radical polymerization by reversible addition-fragmentation chain transfer: the RAFT process. Macromolecules 31:5559–5562

Choi S, Kawauchi S, Ha NY, Takezoe H (2007) Photoinduced chirality in azobenzene-containing polymer systems. Phys Chem Chem Phys 9:3671–3682

Chong YK, Le TP, Moad G, Rizzardo E, Thang SH (1999) A more versatile route to block copolymers and other polymers of complex architecture by living radical polymerization: the RAFT process. Macromolecules 32:2071–2074

Convertine AJ, Lokitz BS, Vasileva Y, Myrick LJ, Scales CW, Lowe AB, Mccormick CL (2006) Direct synthesis of thermally responsive DMA/NIPAM diblock and DMA/NIPAM/DMA triblock copolymers via aqueous, room temperature RAFT polymerization. Macromolecules 39:1724–1730

Corpart P, Charmot D, Biadatti T, Zard S, Michelet D (1998) Block polymer synthesis by controlled radical polymerization. WO9858974

de Witte PAJ, Castriciano M, Cornelissen JJLM, Scolaro LM, Nolte RJM, Rowan AE (2003) Helical polymer-anchored porphyrin nanorods. Chem-Eur J 9:1775–1781

Del Barrio J, Oriol L, Alcala R, Sanchez C (2009) Azobenzene-containing linear-dendritic diblock copolymers by click chemistry: synthesis, characterization, morphological study, and photoinduction of optical anisotropy. Macromolecules 42:5752–5760

Del Barrio J, Oriol L, Sánchez C, Serrano JL, Di Cicco A, Keller P, Li M (2010) Self-assembly of linear-dendritic diblock copolymers: from nanofibers to polymersomes. J Am Chem Soc 132:3762–3769

Del Barrio J, Blasco E, Oriol L, Alcalá R, Sánchez Somolinos C (2013) Diblock copolymer-azobenzene complexes through hydrogen bonding: self-assembly and stable photoinduced optical anisotropy. J Polym Sci A Polym Chem 51:1716–1725

Demus D, Goodby J, Gray GW, Spiess HW, Vill V (1998) Handbook of liquid crystals, vol 3. Wiley-VCH, Weinheim

Discher DE, Eisenberg A (2002) Materials science: soft surfaces: polymer vesicles. Science 297:967–973

Dong C, Liu G (2013) Linear-dendritic biodegradable block copolymers: from synthesis to application in bionanotechnology. Polym Chem 4:46–52

Dong R, Zhu B, Zhou Y, Yan D, Zhu X (2013) Reversible photoisomerization of azobenzene-containing polymeric systems driven by visible light. Polym Chem 4:912–915

Donnio B, Guillon D (2006) Liquid crystalline dendrimers and polypedes. Adv Polym Sci 201:45–155

Donnio B, Buathong S, Bury I, Guillon D (2007) Liquid crystalline dendrimers. Chem Soc Rev 36:1495–1513

Favier A, D'Agosto F, Charreyre M, Pichot C (2004) Synthesis of n-acryloxysuccinimide copolymers by RAFT polymerization, as reactive building blocks with full control of composition and molecular weights. Polymer 45:7821–7830

Ferji K, Nouvel C, Babin J, Albouy PA, Li MH, Six JL (2013) Controlled synthesis of new amphiphilic glycopolymers with liquid crystal grafts. J Polym Sci A Polym Chem 51:3829–3839

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

Finkelmann H, Ringsdorf H, Siol W, Wendorff JH (1978b) Polyreactions in ordered systems, 15. Synthesis of cholesteric liquid crystalline polymers. Makromol Chem 179:829–832

Fletcher ID, Luckhurst GR (1995) The synthesis and characterization of novel non-symmetric dimers with rod-like and disc-like mesogenic units. Liq Cryst 18:175–183

Frechet JMJ (1994) Functional polymers and dendrimers: reactivity, molecular architecture, and interfacial energy. Science 263:1710–1715

Fukuhara K, Fujii Y, Nagashima Y, Hara M, Nagano S, Seki T (2013) Liquid-rystalline polymer and block copolymer domain alignment controlled by free-surface segregation. Angew Chem Int Ed 52:5988–5991

Ganicz T, Makowski T, Stanczyk WA, Tracz A (2012) Side chain polysiloxanes with phthalocyanine moieties. Express Polym Lett 6:373–382

Gao J, Sun Y, Zhou J, Zheng Z, Chen H, Su W, Zhang Q (2007) Preparation of Ag nanoparticles termini-protected side-chain liquid crystalline azobenzene polymers by RAFT polymerization. J Polym Sci A Polym Chem 45:380–5386

Gao L, Zhang C, Liu X, Fan X, Wu Y, Chen X, Shen Z, Zhou Q (2008) Aba type liquid crystalline triblock copolymers by combination of living cationic polymerization and ATRP: synthesis and self-assembly. Soft Matter 4:1230–1236

García T, Larios-López L, Rodríguez-González RJ, Martínez-Ponce G, Solano C, Navarro-Rodríguez D (2012) Liquid-crystalline polymers bearing phenylene (azobenzene) moieties substituted with an electron-donor or electron-acceptor lateral group. Synthesis, mesomorphic behavior and photo-induced isomerization. Polymer 53:2049–2061

García-Amorós J, Velasco D (2012) Recent advances towards azobenzene-based light-driven real-time information-transmitting materials. Beilstein J Org Chem 8:1003–1017

Ge JJ, Zhang A, Mccreight KW, Ho R, Wang S, Jin X, Harris FW, Cheng SZ (1997) Phase structures, transition behaviors, and surface alignment in polymers containing rigid-rodlike backbones with flexible side chains. 1. Monotropic phase behavior in a main-chain/side-chain liquid crystalline polyester. Macromolecules 30:6498–6506

Gemmell PA, Gray GW, Lacey D, Alimoglu AK, Ledwith A (1985) Polymers with rigid anisotropic side groups: 2. Synthesis and properties of some side chain acrylate and methacrylate liquid crystal polymers containing the 4′-alkylbiphenyl-4-yl moiety. Polymer 26:615–621

Gillies ER, Fréchet JM (2002) Designing macromolecules for therapeutic applications: polyester dendrimer poly (ethylene oxide)"bow-tie" hybrids with tunable molecular weight and architecture. J Am Chem Soc 124:14137–14146

Giner I, Haro M, Gascón I, Barrio JD, Carmen López M (2011) Air–water interfacial behavior of linear-dendritic block copolymers containing peg and azobenzene chromophores. J Colloid Interf Sci 359:389–398

Gitsov I (2008) Hybrid linear dendritic macromolecules: from synthesis to applications. J Polym Sci A Polym Chem 46:5295–5314

Gitsov I, Frechet JM (1993) Solution and solid-state properties of hybrid linear-dendritic block copolymers. Macromolecules 26:6536–6546

Gitsov I, Wooley KL, Fréchet JM (1992) Novel polyether copolymers consisting of linear and dendritic blocks. Angew Chem Int Ed 31:1200–1202

Gitsov I, Wooley KL, Hawker CJ, Ivanova PT, Frechet JM (1993) Reactivity of dendritic macromolecules toward linear polymers. Macromolecules 26:5621–5627

Gohy J, Zhao Y (2013) Photo-responsive block copolymer micelles: design and behavior. Chem Soc Rev 42:7117–7129

Goulet Hanssens A, Barrett CJ (2013) Photo-control of biological systems with azobenzene polymers. J Polym Sci A Polym Chem 51:3058–3070

Han D, Tong X, Zhao Y, Zhao Y (2010) Block copolymers comprising π-conjugated and liquid crystalline subunits: induction of macroscopic nanodomain orientation. Angew Chem Int Ed 49:9162–9165

Hao X, Heuts J, Barner Kowollik C, Davis TP, Evans E (2003) Living free-radical polymerization (reversible addition-fragmentation chain transfer) of 6-[4-(4′-methoxyphenyl) phenoxy] hexyl methacrylate: a route to architectural control of side-chain liquid-crystalline polymers. J Polym Sci A Polym Chem 41:2949–2963

Haque HA, Nagano S, Seki T (2012) Lubricant effect of flexible chain in the photoinduced motions of surface-grafted liquid crystalline azobenzene polymer brush. Macromolecules 45:6095–6103

Haque HA, Kekehi S, Hara M, Nagano S, Seki T (2013) High-density liquid-crystalline azobenzene polymer brush attained by surface-initiated ring-opening metathesis polymerization. Langmuir 29:7571–7575

He X, Zhang H, Yan D, Wang X (2003) Synthesis of side-chain liquid-crystalline homopolymers and triblock copolymers with p-methoxyazobenzene moieties and poly (ethylene glycol) as coil segments by atom transfer radical polymerization and their thermotropic phase behavior. J Polym Sci A Polym Chem 41:2854–2864

He X, Sun W, Yan D, Xie M, Zhang Y (2008) Synthesis and characterization of side-chain liquid crystalline abc triblock copolymers with p-methoxyazobenzene moieties by atom transfer radical polymerization. J Polym Sci A Polym Chem 46:4442–4450

He T, Hu T, Zhang X, Zhong G, Zhang H (2009) Synthesis and characterization of a novel liquid crystalline star-shaped polymer based on α-CD core via ATRP. J Appl Polym Sci 112:2120–2126

He Y, He W, Wei R, Chen Z, Wang X (2012) Synthesizing amphiphilic block copolymers through macromolecular azo-coupling reaction. Chem Commun 48:1036–1038

He Y, He W, Liu D, Gu T, Wei R, Wang X (2013) Synthesis of block copolymers via the combination of RAFT and a macromolecular azo coupling reaction. Polym Chem 4:402–406

Hosono N, Kajitani T, Fukushima T, Ito K, Sasaki S, Takata M, Aida T (2010) Large-area three-dimensional molecular ordering of a polymer brush by one-step processing. Science 330:808–811

Hsiue G, Sha Y, Hsieh S, Jeng R, Kuo W (2001) Synthesis and characterization of halogen-containing ferroelectric liquid crystals and side chain liquid crystalline polymers. Liq Cryst 28:365–374

Huang J, Wan D, Huang J (2006) Polymerization of ethyl acrylate using hyperbranched polyglycerol with multi-RAFT groups as chain transfer agent. J Appl Polym Sci 100:2203–2209

Ichimura K (2000) Photoalignment of liquid-crystal systems. Chem Rev 100:1847–1874

Ikeda T, Sasaki T, Ichimura K (1993) Photochemical switching of polarization in ferroelectric liquid-crystal films. Nature 361:428–430

Ikeda T, Mamiya J, Yu Y (2007) Photomechanics of liquid-crystalline elastomers and other polymers. Angew Chem Int Ed 46:506–528

Imrie CT, Inkster RT, Lu Z, Ingram MD (2004) Discotic side group liquid crystal polymer electrolytes. Mol Cryst Liq Cryst 408:33–43

Ishige R, Ishii T, Tokita M, Koga M, Kang S, Watanabe J (2011) Well-ordered lamellar microphase-separated morphology of an ABA triblock copolymer containing a main-chain liquid crystalline polyester as the middle segment. Macromolecules 44:4586–4588

Jin Q, Liu G, Liu X, Ji J (2010) Photo-responsive supramolecular self-assembly and disassembly of an azobenzene-containing block copolymer. Soft Matter 6:5589–5595

Jochum FD, Theato P (2010) Thermo-and light responsive micellation of azobenzene containing block copolymers. Chem Commun 46:6717–6719

Kadota S, Aoki K, Nagano S, Seki T (2005) Photocontrolled microphase separation of block copolymers in two dimensions. J Am Chem Soc 127:8266–8267

Karthaus O, Ringsdorf H, Ebert M, Wendorff JH (1992) Polyesters containing both rodlike and disklike mesogens. Makromol Chem 193:507–513

Kato M, Kamigaito M, Sawamoto M, Higashimura T (1995) Polymerization of methyl methacrylate with the carbon tetrachloride/dichlorotris-(triphenylphosphine) ruthenium (ii)/ methylaluminum bis (2, 6-di-tert-butylphenoxide) initiating system: possibility of living radical polymerization. Macromolecules 28:1721–1723

Kato T, Mizoshita N, Kanie K (2001) Hydrogen-bonded liquid crystalline materials: supramolecular polymeric assembly and the induction of dynamic function. Macromol Rapid Commun 22:797–814

Kato T, Mizoshita N, Kishimoto K (2006) Functional liquid-crystalline assemblies: self-organized soft materials. Angew Chem Int Ed 45:38–68

Kawata K (2002) Orientation control and fixation of discotic liquid crystal. Chem Rec 2:59–80

Kawatsuki N, Matsuda T, Kondo M (2010) Photoinduced orientation of liquid crystalline copolymer films with cinnamic acid side groups synthesized by RAFT polymerization. Mol Cryst Liq Cryst 529:10–19

Keddie DJ (2014) A guide to the synthesis of block copolymers using reversible-addition fragmentation chain transfer (RAFT) polymerization. Chem Soc Rev 43:496–505

Kolb HC, Finn MG, Sharpless KB (2001) Click chemistry: diverse chemical function from a few good reactions. Angew Chem Int Ed 40:2004–2021

Komura M, Iyoda T (2007) AFM cross-sectional imaging of perpendicularly oriented nanocylinder structures of microphase-separated block copolymer films by crystal-like cleavage. Macromolecules 40:4106–4108

Kouwer PHJ, Mehl GH (2009) Hierarchical organisation in shape-amphiphilic liquid crystals. J Mater Chem 19:1564–1575

Kouwer PHJ, Gast J, Jager WF, Mijs WJ, Picken SJ (2001) A series of novel liquid crystalline polymers showing a nematic discotic and/or a nematic columnar phase. Mol Cryst Liq Cryst Sci Technol A 364:225–234

Kouwer PHJ, van den Berg O, Jager WF, Mijs WJ, Picken SJ (2002a) Induced liquid crystalline diversity in molecular and polymeric charge-transfer complexes of discotic mesogens. Macromolecules 35:2576–2582

Kouwer PHJ, Jager WF, Mijs WJ, Picken SJ (2002b) Charge transfer complexes of discotic liquid crystals: a flexible route to a wide variety of mesophases. Macromolecules 35:4322–4329

Kouwer PHJ, Jager WF, Mijs WJ, Picken SJ (2003) Specific interactions in discotic liquid crystals. J Mater Chem 13:458–469

Kreuder W, Ringsdorf H (1983) Liquid crystalline polymers with disk-like mesogens. Makromol Chem Rapid Commun 4:807–815

Kumar S (2004) Recent developments in the chemistry of triphenylene-based discotic liquid crystals. Liq Cryst 31:1037–1059

Kumar S (2005) Triphenylene-based discotic liquid crystal dimers, oligomers and polymers. Liq Cryst 32:1089–1113

Kumar S (2006) Self-organization of disc-like molecules: chemical aspects. Chem Soc Rev 35:83–109

Kumar S (2010) Chemistry of discotic liquid crystals: from monomers to polymers. CRC, Boca Raton

Kumar GS, Neckers DC (1989) Photochemistry of azobenzene-containing polymers. Chem Rev 89:1915–1925

Kumar RM, Saravanan C, Senthil S, Kannan P (2007) Synthesis, characterization and photolysis studies on liquid crystalline poly[4-(4′-x-biphenyl)yl-4″-(m-methacryloyloxyalkyloxy) cinnamate]'s. Eur Polym J 43:2648–2659

Laschat S, Baro A, Steinke N, Giesselmann F, Haegele C, Scalia G, Judele R, Kapatsina E, Sauer S, Schreivogel A, Tosoni M (2007) Discotic liquid crystals: from tailor-made synthesis to plastic electronics. Angew Chem Int Ed 46:4832–4887

Laurent BA, Grayson SM (2006) An efficient route to well-defined macrocyclic polymers via "click" cyclization. J Am Chem Soc 128:4238–4239

Li M, Keller P (2009) Stimuli-responsive polymer vesicles. Soft Matter 5:927–937

Li MH, Keller P, Albouy PA (2003) Novel liquid crystalline block copolymers by ATRP and ROMP. Macromolecules 36:2284–2292

Li Y, He Y, Tong X, Wang X (2005) Photoinduced deformation of amphiphilic azo polymer colloidal spheres. J Am Chem Soc 127:2402–2403

Li Y, He Y, Tong X, Wang X (2006) Stretching effect of linearly polarized Ar+ laser single-beam on azo polymer colloidal spheres. Langmuir 22:2288–2291

Li Z, Zhang Y, Zhu L, Shen T, Zhang H (2010) Efficient synthesis of photoresponsive azobenzene-containing side-chain liquid crystalline polymers with high molecular weights by click chemistry. Polym Chem 1:1501–1511

Lin Y, Chang H, Sheng Y, Tsao H (2012) Photoresponsive polymersomes formed by amphiphilic linear–dendritic block copolymers: generation-dependent aggregation behavior. Macromolecules 45:7143–7156

Liu J, He Y, Wang X (2008) Azo polymer colloidal spheres containing different amounts of functional groups and their photoinduced deformation behavior. Langmuir 24:678–682

Liu J, He Y, Wang X (2009) Size-dependent light-driven effect observed for azo polymer colloidal spheres with different average diameters. Langmuir 25:5974–5979

Liu J, He Y, Wang X (2010) Influence of chromophoric electron-withdrawing groups on photoinduced deformation of azo polymer colloids. Polymer 51:2879–2886

Mahimwalla Z, Yager KG, Mamiya J, Shishido A, Priimagi A, Barrett CJ (2012) Azobenzene photomechanics: prospects and potential applications. Polym Bull 69:967–1006

Matharu AS, Jeeva S, Ramanujam PS (2007) Liquid crystals for holographic optical data storage. Chem Soc Rev 36:1868–1880

Matyjaszewski K, Xia J (2001) Atom transfer radical polymerization. Chem Rev 101:2921–2990

Mayadunne RTA, Jeffery J, Moad G, Rizzardo E (2003) Living free radical polymerization with reversible addition-fragmentation chain transfer (RAFT polymerization): approaches to star polymers. Macromolecules 36:1505–1513

Menghetti S, Alderighi M, Galli G, Tantussi F, Morandini M, Fuso F, Allegrini M (2012) All-optical pulsed writing in azobenzene copolymer films in the sub-millisecond regime. J Mater Chem 22:14510–14517

Meuer S, Braun L, Zentel R (2008) Solubilisation of multi walled carbon nanotubes by α-pyrene functionalised PMMA and their liquid crystalline self-organisation. Chem Commun 27:3166–3168

Moad G, Rizzardo E, Thang SH (2008) Toward living radical polymerization. Acc Chem Res 41:1133–1142

Moad G, Rizzardo E, Thang SH (2009) Living radical polymerization by the RAFT process—a second update. Aust J Chem 62:1402–1472

Moad G, Rizzardo E, Thang SH (2012) Living radical polymerization by the RAFT process—a third update. Aust J Chem 65:985–1076

Morikawa Y, Kondo T, Nagano S, Seki T (2007) Photoinduced 3D ordering and patterning of microphase-separated nanostructure in polystyrene-based block copolymer. Chem Mater 19:1540–1542

Nagano S, Koizuka Y, Murase T, Sano M, Shinohara Y, Amemiya Y, Seki T (2012) Synergy effect on morphology switching: real-time observation of photo-orientation of microphase separation in a block copolymer. Angew Chem Int Ed 51:5884–5888

Natansohn A, Rochon P (1999) Photoinduced motions in azobenzene-based amorphous polymers. Possible photonic devices. Adv Mater 11:1387–1391

Natansohn A, Rochon P (2002) Photoinduced motions in azo-containing polymers. Chem Rev 102:4139–4176

Newkome GR, Yao Z, Baker GR, Gupta VK (1985) Micelles. Part 1. Cascade molecules: a new approach to micelles. A [27]-arborol. J Org Chem 50:2003–2004

Öge T, Zentel R (1996) Manipulation of the ferroelectricity in LC polymers via photomechanical isomerization of azobenzene moieties. Macromol Chem Phys 197:1805–1813

Oliveira ON, Dos Santos DS, Balogh DT, Zucolotto V, Mendonca CR (2005) Optical storage and surface-relief gratings in azobenzene-containing nanostructured films. Adv Colloid Interface Sci 116:179–192

Otmakhova OA, Kuptsov SA, Talroze RV, Patten TE (2003) Preparation of discotic liquid crystal/amorphous block copolymers and evidence for microphase separated amorphous/LC structure. Macromolecules 36:3432–3435

Otsu T, Matsumoto A (1998) Controlled synthesis of polymers using the iniferter technique: developments in living radical polymerization. Adv Polym Sci 136:75–137

Pal SK, Kumar S (2008) Novel triphenylene-based ionic discotic liquid crystalline polymers. Liq Cryst 35:381–384

Pal SK, Setia S, Avinash BS, Kumar S (2013) Triphenylene-based discotic liquid crystals: recent advances. Liq Cryst 40:1769–1816

Patton DL, Taranekar P, Fulghum T, Advincula R (2008) Electrochemically active dendritic-linear block copolymers via RAFT polymerization: synthesis, characterization, and electrodeposition properties. Macromolecules 41:6703–6713

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

Petr M, Hammond PT (2011) Room temperature rapid photoresponsive azobenzene side chain liquid crystal polymer. Macromolecules 44:8880–8885

Reck B, Ringsdorf H (1985) Combined liquid crystalline polymers: mesogens in the main chain and as side groups. Makromol Chem Rapid Commun 6:291–299

Reddy RA, Tschierske C (2006) Bent-core liquid crystals: polar order, superstructural chirality and spontaneous desymmetrisation in soft matter systems. J Mater Chem 16:907–961

Ringsdorf H, Wüstefeld R, Zerta E, Ebert M, Wendorff JH (1989) Induction of liquid crystalline phases: formation of discotic systems by doping amorphous polymers with electron acceptors. Angew Chem Int Ed 28:914–918

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

Rosler A, Vandermeulen GWM, Klok H (2001) Advanced drug delivery devices via self-assembly of amphiphilic block copolymers. Adv Drug Deliv Rev 53:95–108

Royes J, Rebolé J, Custardoy L, Gimeno N, Oriol L, Tejedor RM, Piñol M (2012) Preparation of side-chain liquid crystalline azopolymers by CuAAC postfunctionalization using bifunctional azides: induction of chirality using circularly polarized light. J Polym Sci A Polym Chem 50:1579–1590

Scheerder J, Marcelis A, Achten R, Sudhölter EJ (2000) Synthesis and thermotropic properties of novel side-chain dimer liquid crystalline polymers. Macromol Chem Phys 201:1303–1310

Schrock RR (1990) Living ring-opening metathesis polymerization catalyzed by well-characterized transition-metal alkylidene complexes. Acc Chem Res 23:158–165

Semsarilar M, Sébastien P (2010) 'Green' reversible addition-fragmentation chain-transfer (RAFT) polymerization. Nat Chem 2:811–820

Sergeyev S, Pisula W, Geerts YH (2007) Discotic liquid crystals: a new generation of organic semiconductors. Chem Soc Rev 36:1902–1929

Shen G, Xue G, Cai J, Zou G, Li Y, Zhang Q (2013) Photo-induced reversible uniform to Janus shape change of vesicles composed of PNIPAM-b-PAzPy2. Soft Matter 9:2512–2517

Shi Z, Lu H, Chen Z, Cheng R, Chen D (2012a) Rational design, syntheses, characterization and solution behavior of amphiphilic azobenzene-containing linear-dendritic block copolymers. Polymer 53:359–369

Shi Z, Chen D, Lu H, Wu B, Ma J, Cheng R, Fang J, Chen X (2012b) Self-assembled hierarchical structure evolution of azobenzene-containing linear-dendritic liquid crystalline block copolymers. Soft Matter 8:6174–6184

Shibaev VP, Kostromin SG, Plate NA (1982) Thermotropic liquid-crystalline polymers—VI: comb-like liquid-crystalline polymers of the smectic and nematic types with cyanobiphenyl groups in the side-chains. Eur Polym J 18:651–659

Stamenović MM, Espeel P, Baba E, Yamamoto T, Tezuka Y, Du Prez FE (2013) Straightforward synthesis of functionalized cyclic polymers in high yield via RAFT and thiolactone–disulfide chemistry. Polym Chem 4:184–193

Stenzel MH, Davis TP (2002) Star polymer synthesis using trithiocarbonate functional β-cyclodextrin cores (reversible addition-fragmentation chain-transfer polymerization). J Polym Sci A Polym Chem 40:4498–4512

Stillings C, Pettau R, Wendorff JH, Schmidt HW, Kreger K (2010) Lamellar nanoconfinements effects in discotic liquid crystalline block copolymers. Macromol Chem Phys 211:250–258

Su W, Luo Y, Yan Q, Wu S, Han K, Zhang Q, Gu Y, Li Y (2007) Photoinduced fusion of micro-vesicles self-assembled from azobenzene-containing amphiphilic diblock copolymers. Macromol Rapid Commun 28:1251–1256

Sun B, Zhu X, Zhu J, Cheng Z, Zhang Z (2007) A novel synthetic method for well-defined polymers containing benzotriazole and diazobenzene chromophores. Macromol Chem Phys 208:1101–1109

Szwarc M, Levy M, Milkovich R (1956) Polymerization initiated by electron transfer to monomer. A new method of formation of block polymers1. J Am Chem Soc 78:2656–2657

Tahar-Djebbar I, Nekelson F, Heinrich B, Donnio B, Guillon D, Kreher D, Mathevet F, Attias A (2011) Lamello-columnar mesophase formation in a side-chain liquid crystal π-conjugated polymer architecture. Chem Mater 23:4653–4656

Talroze RV, Otmakhova OA, Koval MA, Kuptsov SA, Platé NA, Finkelmann H (2000) Acrylate based polymers and networks containing triphenylene groups: synthesis and structures. Macromol Chem Phys 201:877–881

Tang X, Gao L, Fan X, Zhou Q (2007a) ABA-type amphiphilic triblock copolymers containing p-ethoxy azobenzene via atom transfer radical polymerization: synthesis, characterization, and properties. J Polym Sci A Polym Chem 45:2225–2234

Tang X, Gao L, Fan X, Zhou Q (2007b) Effect of the terminal substituent of azobenzene on the properties of ABA triblock copolymers via atom transfer radical polymerization. J Polym Sci A Polym Chem 45:5190–5198

Thünemann AF, Ruppelt D, Ito S, Mullen K (1999) Supramolecular architecture of a functionalized hexabenzocoronene and its complex with polyethyleneimine. J Mater Chem 9:1055–1057

Thünemann AF, Kubowicz S, Burger C, Watson MD, Tchebotareva N, Muellen K (2003) A-helical-within-discotic columnar structures of a complex between poly(ethylene oxide)-block-poly(l-lysine) and a hexa-peri-hexabenzocoronene. J Am Chem Soc 125:352–356

Tian Y, Watanabe K, Kong X, Abe J, Iyoda T (2002) Synthesis, nanostructures, and functionality of amphiphilic liquid crystalline block copolymers with azobenzene moieties. Macromolecules 35:3739–3747

Tomalia DA, Baker H, Dewald J, Hall M, Kallos G, Martin S, Roeck J, Ryder J, Smith P (1985) A new class of polymers: starburst-dendritic macromolecules. Polym J 17:117–132

Tomatsu I, Hashidzume A, Harada A (2005) Photoresponsive hydrogel system using molecular recognition of α-cyclodextrin. Macromolecules 38:5223–5227

Trimmel G, Riegler S, Fuchs G, Slugovc C, Stelzer F (2005) Liquid crystalline polymers by metathesis polymerization. Adv Polym Sci 176:43–87

Van der Pol JF, Neeleman E, Nolte RJ, Zwikker JW, Drenth W (1989) Asymmetrically substituted liquid-crystalline phthalocyanines and side-chain polymers derived from them. Die Makromol Chem 190:2727–2745

Vapaavuori J, Valtavirta V, Alasaarela T, Mamiya J, Priimagi A, Shishido A, Kaivola M (2011) Efficient surface structuring and photoalignment of supramolecular polymer–azobenzene complexes through rational chromophore design. J Mater Chem 21:15437–15441

Viswanathan NK, Kim DY, Bian S, Williams J, Liu W, Li L, Samuelson L, Kumar J, Tripathy SK (1999) Surface relief structures on azo polymer films. J Mater Chem 9:1941–1955

Voigt-Martin IG, Simon P, Bauer S, Ringsdorf H (1995) Structure and defects in sanidic liquid crystalline polymers. 1. Macromolecules 28:236–242

Wang J, Matyjaszewski K (1995) Controlled/"living" radical polymerization. Atom transfer radical polymerization in the presence of transition-metal complexes. J Am Chem Soc 117:5614–5615

Wang R, Wang Z (2010) Theory of side-chain liquid crystal polymers: bulk behavior and chain conformation. Macromolecules 43:10096–10106

Wang D, Wang X (2013) Amphiphilic azo polymers: molecular engineering, self-assembly and photoresponsive properties. Prog Polym Sci 38(2):271–301

Wang X, Zhou Q (2004) Liquid crystalline polymers. World Scientific, Singapore

Wang X, Kumar J, Tripathy SK, Li L, Chen J, Marturunkakul S (1997a) Epoxy-based nonlinear optical polymers from post azo coupling reaction. Macromolecules 30:219–225

Wang X, Chen J, Marturunkakul S, Li L, Kumar J, Tripathy SK (1997b) Epoxy-based nonlinear optical polymers functionalized with tricyanovinyl chromophores. Chem Mater 9:45–50

Wang D, Ye G, Wang X (2007) Synthesis of aminoazobenzene-containing diblock copolymer and photoinduced deformation behavior of its micelle-like aggregates. Macromol Rapid Commun 28:2237–2243

Wang D, Liu J, Ye G, Wang X (2009) Amphiphilic block copolymers bearing strong push–pull azo chromophores: synthesis, micelle formation and photoinduced shape deformation. Polymer 50:418–427

Wang L, Li K, Lin H (2010) Synthesis and characterization of side-chain liquid-crystalline block-copolymers containing laterally attached photoluminescent quinquephenyl units via ATRP. Polymer 51:75–83

Wang Q, Yang C, Xie H, Wang X, Zhang H (2010) Effect of mesogenic density on liquid-crystalline behaviours of polymethacrylates bearing azobenzene mesogen. Liq Cryst 37:435–443

Wang S, Shen Q, Nawaz MH, Zhang W (2013) Photocontrolled reversible supramolecular assemblies of a diblock azo-copolymer based on β-cyclodextrin–azo host–guest inclusion complexation. Polym Chem 4:2151–2157

Weck M, Mohr B, Maughon BR, Grubbs RH (1997) Synthesis of discotic columnar side-chain liquid crystalline polymers by ring-opening metathesis polymerization (POMP). Macromolecules 30:6430–6437

Werth M, Spiess HW (1993) The role of the spacer in discotic polymers. Makromol Chem Rapid Commun 14:329–338

Wu S, Wang L, Kroeger A, Wu Y, Zhang Q, Bubeck C (2011) Block copolymers of PS-b-PEO co-assembled with azobenzene-containing homopolymers and their photoresponsive properties. Soft Matter 7:11535–11545

Wu B, Mu B, Wang S, Duan J, Fang J, Cheng R, Chen D (2013) Triphenylene-based side chain liquid crystalline block copolymers containing a PEG block: controlled synthesis, microphase structures evolution and their interplay with discotic mesogenic orders. Macromolecules 46:2916–2929

Wurm F, Frey H (2011) Linear–dendritic block copolymers: the state of the art and exciting perspectives. Prog Polym Sci 36:1–52

Xia Y, Verduzco R, Grubbs RH, Kornfield JA (2008) Well-defined liquid crystal gels from telechelic polymers. J Am Chem Soc 130:1735–1740

Xiang Y, Xue X, Zhu J, Zhang Z, Zhang W, Zhou N, Zhu X (2010) Fluorescence behavior of an azobenzene-containing amphiphilic diblock copolymer. Polym Chem 1:1453–1458

Xie H, Liu Y, Zhong G, Zhang H, Chen E, Zhou Q (2009) Design, synthesis, and multiple hierarchical ordering of a novel side-chain liquid crystalline-rod diblock copolymer. Macromolecules 42:8774–8780

Xing C, Lam JW, Zhao K, Tang BZ (2008) Synthesis and liquid crystalline properties of poly (1-alkyne)s carrying triphenylene discogens. J Polym Sci A Polym Chem 46:2960–2974

Yan B, Tong X, Ayotte P, Zhao Y (2011) Light-responsive block copolymer vesicles based on a photo-softening effect. Soft Matter 7:10001–10009

Yan Q, Xin Y, Zhou R, Yin Y, Yuan J (2011) Light-controlled smart nanotubes based on the orthogonal assembly of two homopolymers. Chem Commun 47:9594–9596

Yang C, Wang Q, Xie H, Zhong G, Zhang H (2010) Synthesis and characterisation of polymethacrylates containing para-, meta-and ortho-monosubstituted azobenzene moieties in the side chain. Liq Cryst 37:1339–1346

Yesodha SK, Sadasivan Pillai CK, Tsutsumi N (2004) Stable polymeric materials for nonlinear optics: a review based on azobenzene systems. Prog Polym Sci 29:45–74

Yu H (2014) Recent advances in photoresponsive liquid-crystalline polymers containing azobenzene chromophores. J Mater Chem C 2:3047–3054

Yu D, Vladimirov N, Fréchet JM (1999) MALDI-TOF in the characterizations of dendritic-linear block copolymers and stars. Macromolecules 32:5186–5192

Yu WH, Kang ET, Neoh KG (2004) Functionalization of hydrogen-terminated Si(100) substrate by surface-initiated RAFT polymerization of 4-vinylbenzyl chloride and subsequent derivatization for photoinduced metallization. Ind Eng Chem Res 43:5194–5202

Yu H, Iyoda T, Ikeda T (2006a) Photoinduced alignment of nanocylinders by supramolecular cooperative motions. J Am Chem Soc 128:11010–11011

Yu H, Li J, Ikeda T, Iyoda T (2006b) Macroscopic parallel nanocylinder array fabrication using a simple rubbing technique. Adv Mater 18:2213–2215

Yu H, Asaoka S, Shishido A, Iyoda T, Ikeda T (2007) Photoinduced nanoscale cooperative motion in a well-defined triblock copolymer. Small 3:768–771

Yu Z, Lam JW, Zhao K, Zhu C, Yang S, Lin J, Li BS, Liu J, Chen E, Tang BZ (2013) Mesogen jacketed liquid crystalline polyacetylene containing triphenylene discogen: synthesis and phase structure. Polym Chem 4:996–1005

Zeng D, Tahar-Djebbar I, Xiao Y, Kameche F, Kayunkid N, Brinkmann M, Guillon D, Heinrich B, Donnio B, Ivanov DA (2014) Intertwined lamello-columnar coassemblies in liquid-crystalline side-chain π-conjugated polymers: toward a new class of nanostructured supramolecular organic semiconductors. Macromolecules 47:1715–1731

Zhang Y, Zhang W, Chen X, Cheng Z, Wu J, Zhu J, Zhu X (2008) Synthesis of novel three-arm star azo side-chain liquid crystalline polymer via ATRP and photoinduced surface relief gratings. J Polym Sci A Polym Chem 46:777–789

Zhang X, Boissé S, Bui C, Albouy P, Brûlet A, Li M, Rieger J, Charleux B (2012) Amphiphilic liquid-crystal block copolymer nanofibers via RAFT-mediated dispersion polymerization. Soft Matter 8:1130–1141

Zhao Y, He J (2009) Azobenzene-containing block copolymers: the interplay of light and morphology enables new functions. Soft Matter 5:2686–2693

Zhao Y, Ikeda T (2009) Smart light-responsive materials: azobenzene-containing polymers and liquid crystals. John Wiley & Sons, New Jersey

Zhao Y, Qi B, Tong X, Zhao Y (2008) Synthesis of double side-chain liquid crystalline block copolymers using RAFT polymerization and the orientational cooperative effect. Macromolecules 41:3823–3831

Zhou M, Han CD (2005) Synthesis and characterization of a combined main-chain/side-chain liquid-crystalline polymer exhibiting both thermotropic and lyotropic characteristics and its lyotropic phase behavior. Macromolecules 38:9602–9609

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

Zhou Y, Ahn S, Lakhman RK, Gopinadhan M, Osuji CO, Kasi RM (2011) Tailoring crystallization behavior of PEO-based liquid crystalline block copolymers through variation in liquid crystalline content. Macromolecules 44:3924–3934

Zhu Y, Wang X (2013) Synthesis and photoresponsive properties of two liquid crystalline polymers bearing branched azobenzene-containing side chains. Polym Chem 4:5108–5118

Zhu Y, Guan X, Shen Z, Fan X, Zhou Q (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 Z, Zou DC, Sun PC, Fan XH, Zhou QF (2014) 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 A Polym Chem 52:295–304

Zou G, Jiang H, Zhang Q, Kohn H, Manaka T, Iwamoto M (2010) Chiroptical switch based on azobenzene-substituted polydiacetylene 1D films under thermal and photic stimuli. J Mater Chem 20:285–291