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主链型手性液晶弹性体(特邀)

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摘 要:主链型手性液晶弹性体是一类具有周期性纳米结构的软光子晶体,包括一维胆甾相液晶弹性体和三维蓝相液晶弹性体,不仅可以选择性反射圆偏振光,还能够灵敏地响应外界环境的变化,在自适应光学、变色伪装、信息加密和智能隐身等领域有着广泛的应用前景。随着新型材料体系和先进制备技术的发展,研究人员近年来提出了多种不同的策略,设计和制备具有手性纳米超结构的液晶弹性体,并深入研究了手性液晶弹性体的性能及潜在应用。本文系统综述了主链型手性液晶弹性体的设计、制备和应用进展,重点介绍了一维胆甾相液晶弹性体的平行取向法、各向异性挥发法、刮涂法、3D 打印,以及无需额外取向的蓝相液晶弹性体三维纳米自组装方法,并总结讨论了主链型手性液晶弹性体存在的挑战以及未来发展方向。

关键词:手性液晶弹性体;主链型液晶;光子晶体;胆甾相液晶;蓝相液晶

中图分类号: TG147

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0 引言

液晶是一种介于液态与结晶态之间的智能软材料,兼具液体的流动性和晶体的有序性,自 19 世纪末被发现以来^[1],一直受到人们的广泛关注。近几十年,显示技术中低分子量液晶的广泛使用,推动了液晶材料在其他领域研究应用的迅速发展,包括太阳能捕获^[2-3]、智能光子学^[4-7]和生物医学^[8-9]等方面。液晶聚合物是由液晶分子发生聚合反应或接枝在柔性聚合物主链上得到的一类功能性先进高分子材料,按照不同的化学组成、交联方式,可分为液晶聚合物网络(Liquid Crystal Networks, LCNs)和液晶弹性体(Liquid Crystal Elastomers, LCEs)^[10-12]。液晶聚合物网络具有由液晶单体聚合得到的中度到密集交联的网络结构。液晶弹性体是将聚合物熵弹性和液晶自组织特性结合起来的功能材料,与含有较高交联密度的液晶聚合物网络相比,液晶弹性体主链通常是柔性的,总的交联密度较低,当受到外界刺激时,液晶弹性体的取向排列会发生很大的变化。这种液晶基元相对于聚合物网络发生旋转的性质使其具有许多独特的行为,例如应力-光学效应,利用向列相-各向同性相转变的单轴驱动,准静态和动态加载下的软应力响应,在一定的温度、频率和加载速率范围内表现出的增强耗散等^[13-17]。根据液晶基元在大分子网络中所处位置的不同,可将液晶弹性体分为主链型和侧链型。主链型液晶弹性体(Main-chain Liquid Crystal Elastomers, MLCEs)的液晶单元处于聚合物分子主链上,与以侧链构型并入聚合物支链上相比,MLCEs 具有更高的链各向异性,在受到外界刺激时,产生较大的可逆性形变,并且具有很高的能量密度,这些优异的性能使其广泛应用于智能驱动器、软体机器人、人工肌肉和自调节器件等领域^[18-32]。

将手性分子引入主链型向列相液晶弹性体中,可自组装形成具有周期性纳米结构的手性软光子晶体^[33-35],如一维胆甾相液晶弹性体(Cholesteric Liquid Crystal Elastomers, CLCEs)和三维蓝相液晶弹性体(Blue Phase Liquid Crystal Elastomers, BPLCEs)。胆甾相液晶弹性体具有一维手性螺旋结构,分子自组装

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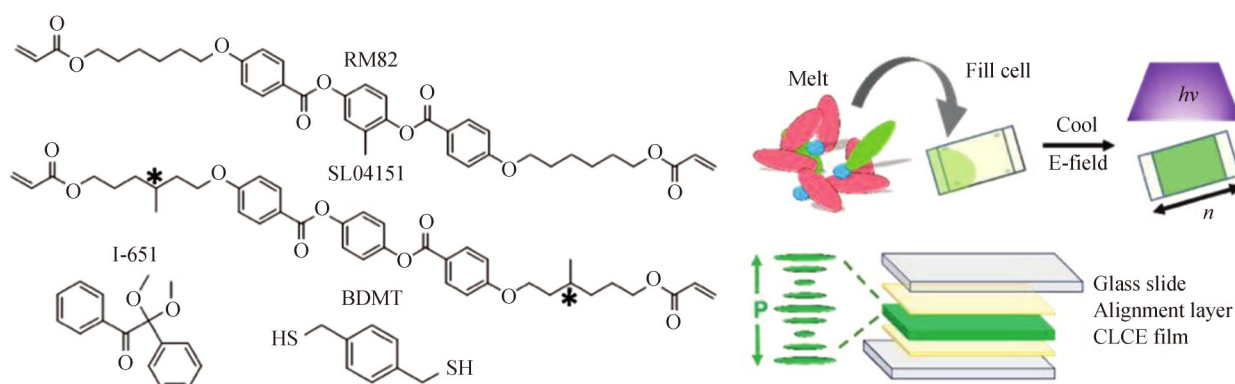
形成螺距(周期)为几百纳米的超分子螺旋排列,选择性反射与螺旋结构具有相同旋向的圆偏振光,光的波长由螺距和平均折射率决定^[36-39]。蓝相液晶弹性体具有三维光子晶体结构,液晶分子以双扭曲的形态排列,形成的双扭曲圆柱体相互叠加堆积成两种具有体心立方对称或简单立方对称的周期性三维立方晶格,并呈现出较窄的光子带隙^[40-42]。由于其固有的液晶性质,这类手性液晶弹性体不仅可以选择性反射圆偏振光,还能够灵敏地响应力、热、电、光、湿度等刺激变化,呈现出结构色的动态调控,在变色伪装、信息加密、可调谐激光等领域具有广泛的应用前景^[43-47]。

近年来,随着手性液晶材料体系的不断发展,科研人员提出了多种不同的策略构筑具有手性自组装纳米结构的液晶弹性体,以制备具有均匀结构色、宽光谱反射范围、良好机械性能并可大面积加工的手性液晶软光子晶体。本文根据液晶材料体系和制备方法的不同,总结了主链型手性液晶弹性体的研究进展,重点介绍了胆甾相液晶弹性体的平行取向法、各向异性挥发法、刮涂法、3D打印法以及无需取向层的蓝相液晶三维自组装方法,系统介绍了近年来手性液晶弹性体的设计、制备及应用研究进展,并进一步讨论了手性液晶功能材料未来的发展方向。

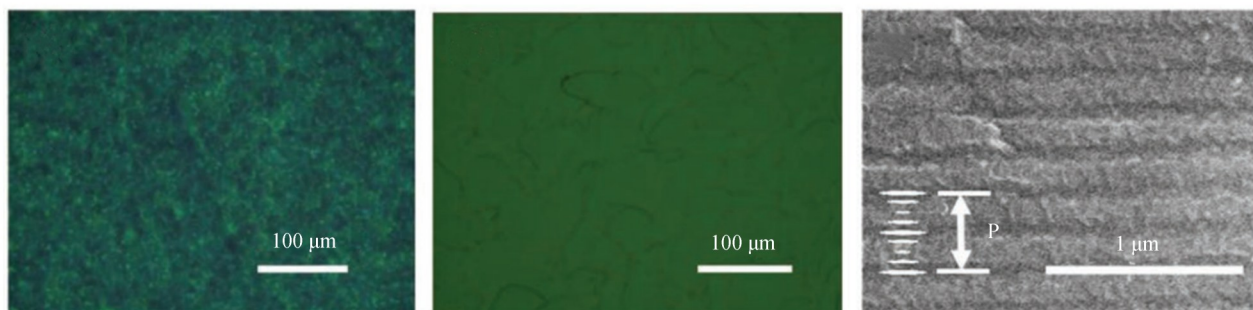
1 主链型胆甾相液晶弹性体的制备

1.1 平行取向法

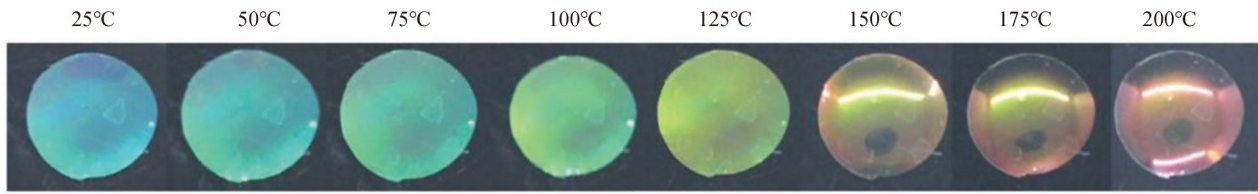
平行取向法^[48-54]通常首先制备玻璃表面经过平行取向处理(摩擦取向或光取向)的液晶盒,将液晶单体、扩链剂、催化剂等按一定比例反应形成低聚物,或直接与光引发剂等混合均匀,通过毛细力作用注入液晶盒中。液晶分子与取向涂层相互作用,通过拓扑俘获^[55]强化取向,将液晶分子锚定在这些表面附近,在手性剂的作用下自组装形成螺旋结构,经紫外光照或施加温度场发生自由基聚合反应,得到具有交联结构的主链型手性液晶弹性体。例如,WHITE T J等^[56]利用场控制和表面光取向的方法,制备了取向良好(单畴)的胆甾相液晶弹性体,如图1(a)、(b),该弹性体具有较强的热机械耦合和较大的尺度响应。在可见光谱范围内,胆甾相液晶弹性体的选择性反射波长可以通过温度连续调节,调节范围可达200 nm以上,如图1(c)所示,研究发现该性能与CLCE膜厚度方向上的热机械膨胀直接相关。通过在体系中引入光敏手性掺杂剂,使胆甾相螺距分布不均一,CLCE的选择性反射带宽可增加到200 nm以上。胆甾相液晶膜的布拉格反射波长在热的作用下可从可见光区调制到红外光区。值得一提的是,作者将CLCE膜与取向的LCE层压结合,发现当



(a) Schematic illustration of molecular structure and preparation process of CLCEs



(b) Polarized image of CLCEs prepared without and with an applied field and the SEM image of a cross section of the film



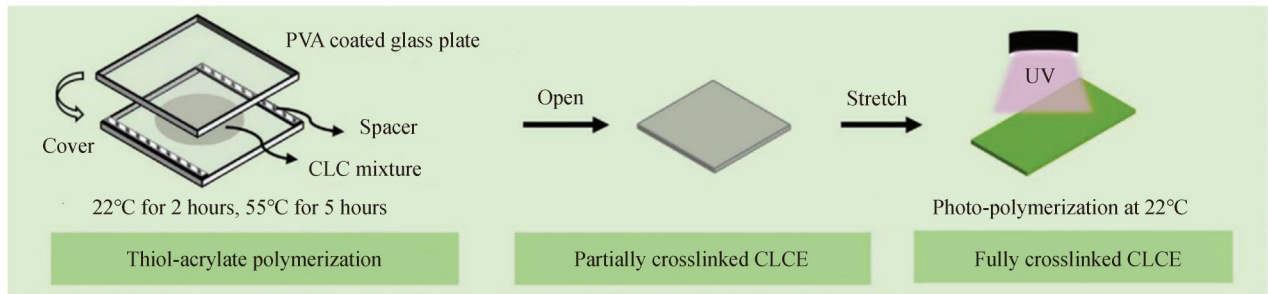
(c) Thermochromism in a representative CLCE film upon heating from 25 to 200°C

图1 利用场控制和表面光取向制备液晶弹性体^[56]

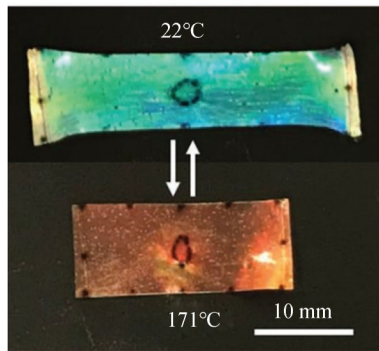
Fig. 1 Preparation of CLCEs via a synthesis procedure leveraging field-enforced and surface directed alignment^[56]

向列相液晶弹性体发生机械变形时,CLCE由于热致变色响应会产生具有镜面反射和漫反射同时变化的固态元件。该研究展示了液晶弹性体具有独特的光调控能力,在纺织、光学和建筑节能等领域具有潜在的应用。

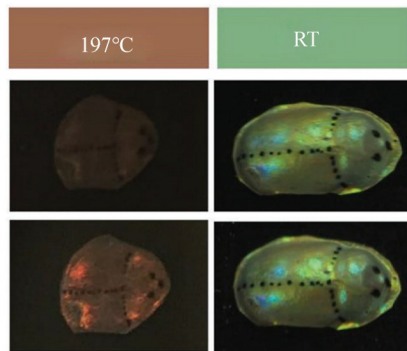
利用胆甾相液晶弹性体平行取向法,SCHENNING A P H J等^[57]制备了一种兼具变形和变色功能的4D光子软体驱动器。如图2(a)所示,作者采用两步法,首先将液晶前驱体混合均匀,在各向同性温度下注入含有摩擦取向聚乙烯醇层的液晶盒,待迈克尔加成反应结束后,将得到的部分交联的胆甾相液晶薄膜进行机



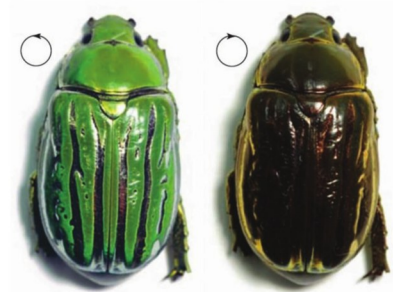
(a) The two-step crosslinking procedure to prepare the temperature responsive cholesteric liquid crystal elastomer film



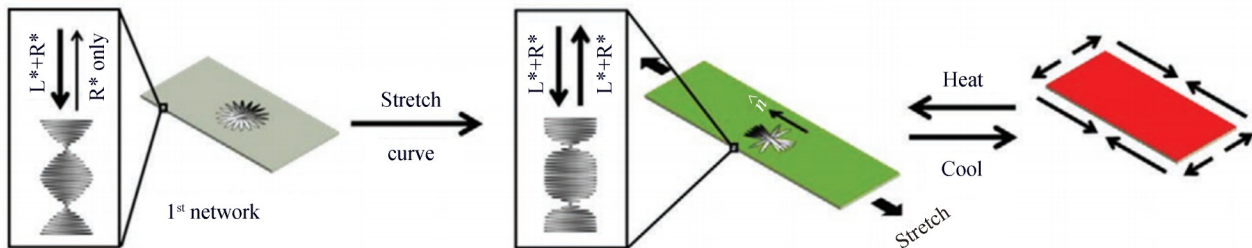
(b) The photographs of the film at different temperatures



(c) Photographs of programmed CLCEs viewed with LCP and RCP at different temperatures



(d) Photographs of the beetle *C. gloriosa* viewed with LCP and RCP



(e) Schematic illustration of the shape and color change of the film. L*: left-handed circularly polarized light, R*: right-handed circularly polarized light. The newly formed alignment director after stretching is indicated as \hat{n}

图2 具有可切换超反射率的4D手性光子驱动器^[57]

Fig. 2 4D chiral photonic actuators with switchable hyper-reflectivity^[57]

械拉伸,然后通过紫外光诱发自由基原位聚合进一步固定拉伸编程的液晶螺旋结构。如图2(b)所示,编程后的CLCE薄膜在温度驱动下其颜色和形状均可以在编程态和原始形状之间可逆地发生转变。采用模塑的方法,作者制备了具有圆偏振结构色的三维甲虫模型,如图2(c)、(d)。当温度改变时,这种仿生甲虫手性液晶弹性体能够同时改变自身的形状、颜色和圆偏振反射。这是由于力的作用使螺旋结构变形,产生扭曲的螺旋结构,同时反射左旋和右旋圆偏振光,如图2(e)所示。加热后,薄膜回到螺旋结构状态,薄膜的偏振选择性可逆地从反射等量左右偏振光转变为只反射右偏振光。该研究提供了一种简单的方式来制备具有任意3D形状和可编程反射、颜色和形状变化的生物启发的刺激响应多功能材料,在传感驱动器、可切换超反射薄膜等领域存在广泛的应用。

YANG Shu 等^[58]采用两步法开发了一种气体驱动主链型手性液晶弹性体薄膜,首先使用手性向列相溶剂稳定液晶预聚物,然后光聚合液晶预聚物并去除手性向列相溶剂。如图3(a)和(b)所示,作者将得到的胆

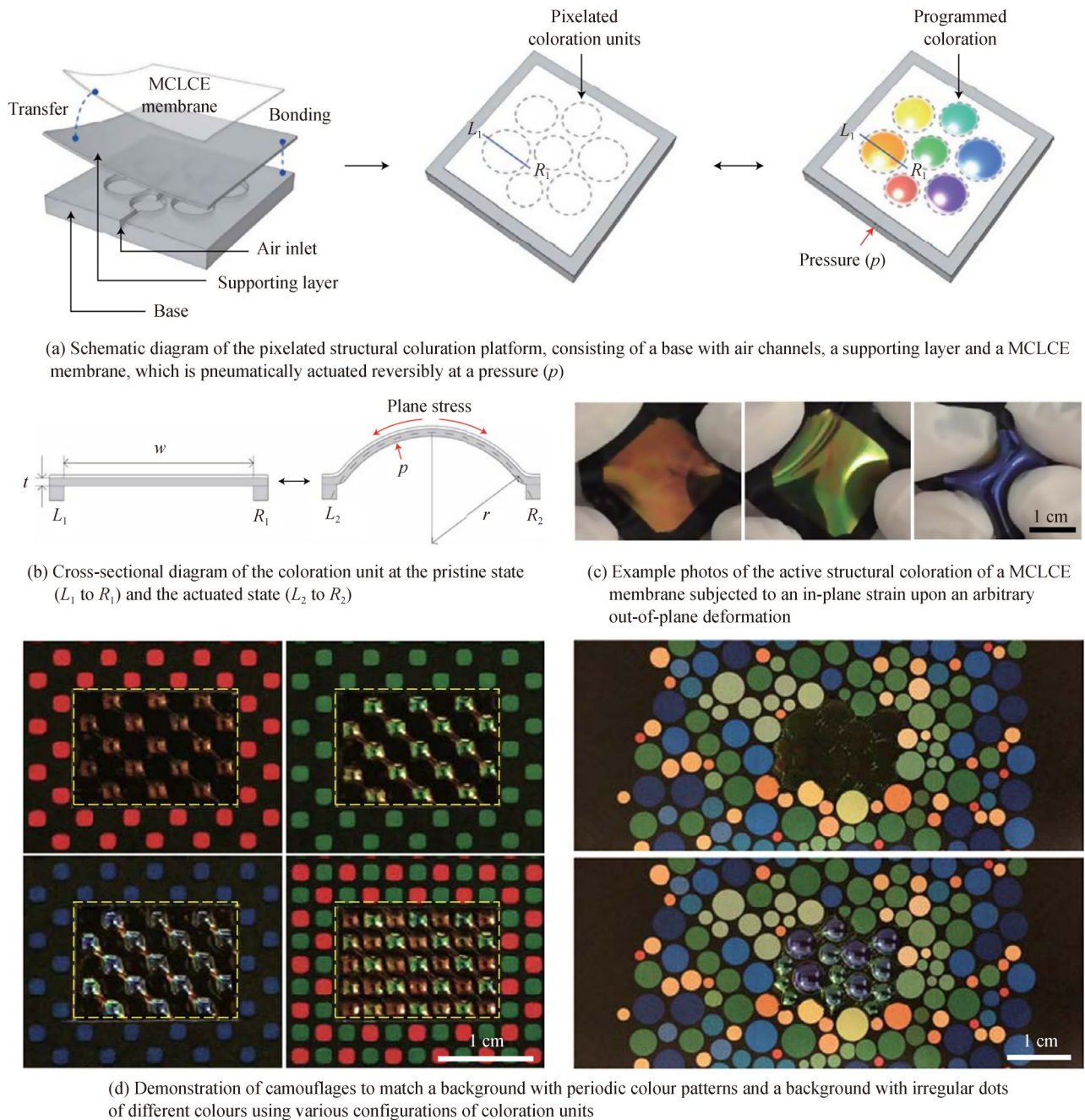


图3 气动手性向列相液晶弹性体的宽光谱和像素化伪装^[58]

Fig. 3 Broadband and pixelated camouflage in inflating chiral nematic liquid crystalline elastomers^[58]

胆甾相液晶薄膜与聚二甲基硅氧烷支撑层组成双层着色单元,着色单元具有较高的弹性各向异性和超大泊松比(>0.5),垂直方向上相对小的应变可引起周期性的大变形。作者进一步利用这些性质对封装空气通道的尺寸和布局进行了几何编程,实现了从近红外(800 nm)到紫外波长(350 nm)的宽反射颜色调控,如图3(c),该复合薄膜具有小于20%的高保真等双轴横向应变,对于实现手性液晶弹性体的快速和像素化显示有重要意义。为了探索胆甾相液晶弹性体薄膜的潜在应用,作者嵌入了多个独立的空气通道以进行多路可控变色,展示了在具有周期性或不规则颜色图案背景下的变色隐身。如图3(d)所示,无论是在周期性图案还是不规则图案背景下,每个通道都可以作为颜色“像素”实现单独控制。这种基于手性液晶弹性体的变色材料可用于密码学、自适应光学、软机器人和智能光子皮肤等领域。

受变色龙皮肤变色功能的启发,BOWMAN C N等^[59]设计并制备了具有可重构、空间可编程和光响应特性的共价自适应胆甾相液晶弹性体变色龙皮肤。如图4(a)和(c)所示,作者将液晶前驱体注入液晶盒中,在60 °C反复加热条件下通过手动剪切的方式取向,之后进行可见光(400~500 nm)聚合。研究发现,在应力的作用下,胆甾相液晶弹性体螺距减小导致其圆偏振反射色发生蓝移,如图4(b)。由于引入了可发生加成

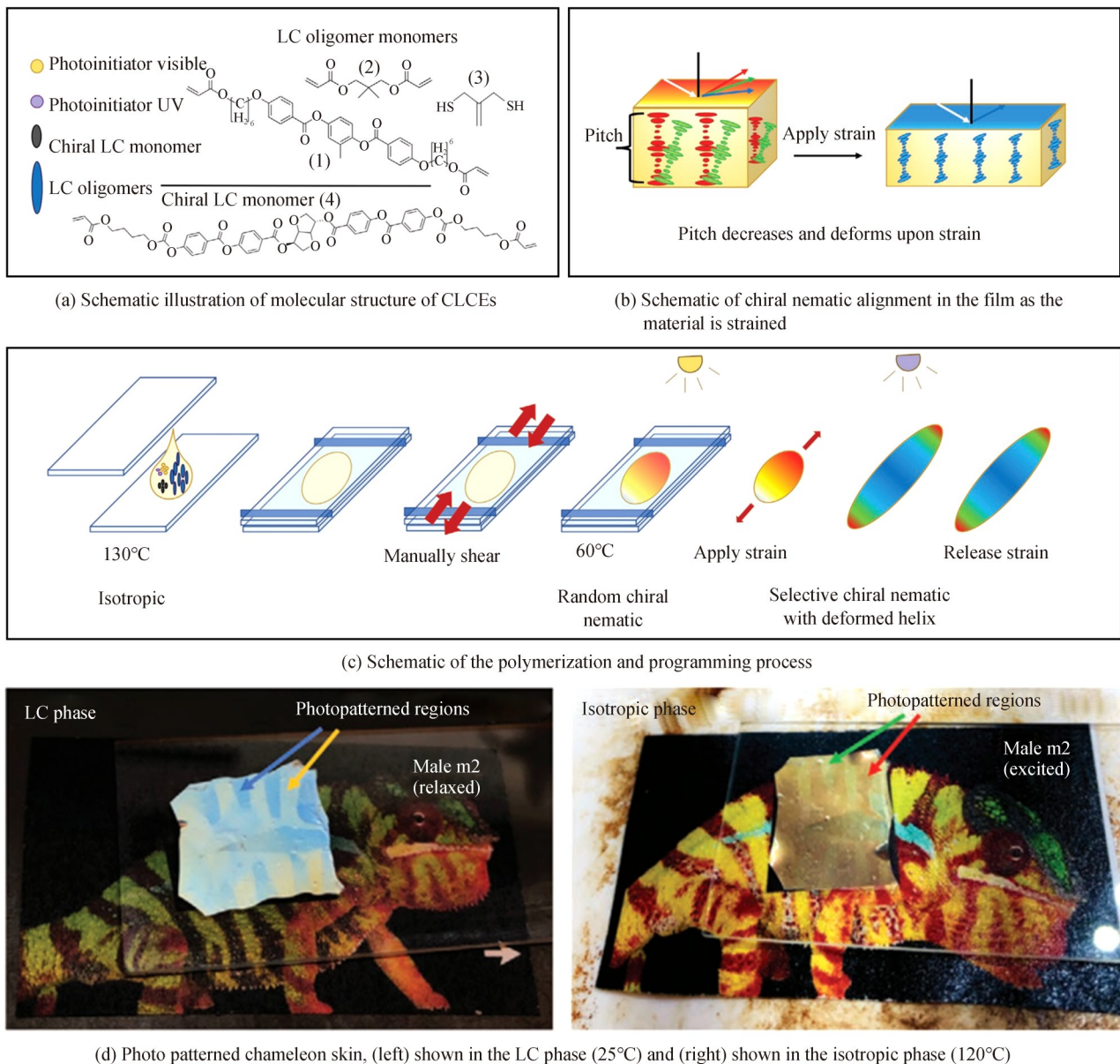


图4 可重构、空间可编程和具有光响应的共价自适应胆甾相液晶弹性体^[59]

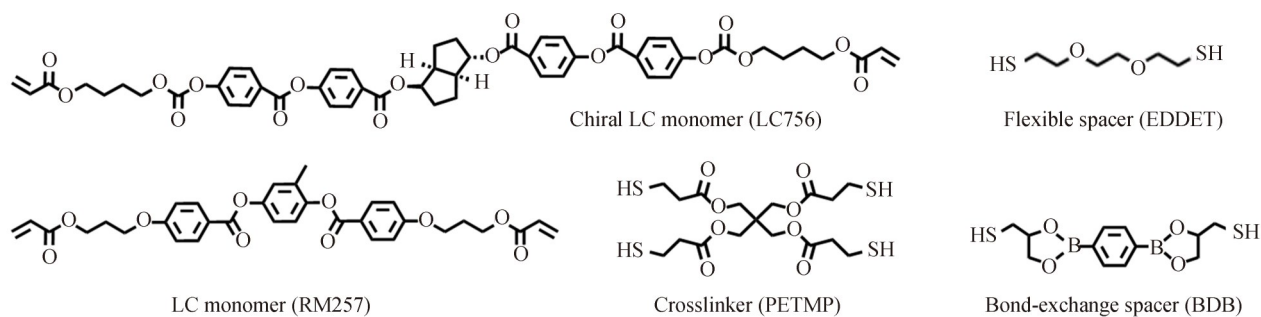
Fig. 4 Reconfigurable, spatially programmable and photoresponsive covalent adaptive cholesteric liquid crystal elastomers^[59]

断裂链转移反应的烯丙基硫分子,交联后的胆甾相液晶弹性体薄膜可在紫外光下进行键交换反应,实现共价网络结构的重排。基于此,作者对动态共价自适应 CLCE 进行了一系列形状及颜色编程。通过使用条纹状的光掩膜,CLCE 被选择性地图案化,得到明显的蓝移图案,加热后,图案区域发生红移,但由于它们不能完全回复到初始状态,与没有图案的红色区域相比,这些线条呈现出黄/绿圆偏振反射色。利用这一策略,作者展示了一种模拟变色龙皮肤图案的人工变色龙皮肤,如图 4(d),在变色龙的“松弛”状态下,图案呈现出蓝色和黄色,但当材料加热到各向同性阶段时,变色龙处于“受激”状态呈现绿色和红色,这在信号传递或伪装时有重要应用。

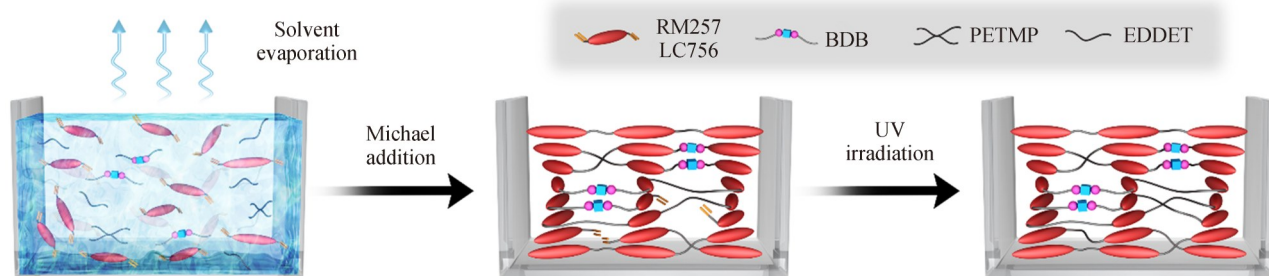
1.2 各向异性挥发法

2001年, FINKELMANN H^[60]提出了“各向异性挥发”策略制备具有螺旋自组装结构的胆甾相液晶弹性体薄膜。作者将前驱体溶液在高温下连续离心 10 h,前半段进行硅氢化反应,后半段进行溶剂蒸发。虽然通过这种方式产生了满意的效果,并且随后优化实验方案将离心时间缩短至 5~8 h,但该方法很繁琐,而且不适用于大规模制备。受到硫醇-丙烯酸酯 Michael 加成和光聚合反应两步法制备主链型向列相液晶弹性体的启发^[61], LAGERWALL J P F 等^[62]通过引入双丙烯酸酯手性分子实现了主链型胆甾相液晶弹性体的合成。该方法操作简单、条件温和,易于大规模制备颜色均匀的 CLCE 薄膜,得到的主链型胆甾相液晶弹性体具有强烈的圆偏振反射颜色,可通过拉伸或压缩在整个可见光谱中重复、快速和连续地调节。该方法没有使用离心、取向层、外部磁场或电场来对样品进行取向,而是利用了溶剂的各向异性挥发。前驱体混合物中丙烯酸酯和硫醇的初始“点击”聚合反应形成的凝胶,强烈地附着在基材上,当溶剂蒸发时,它不能在横向尺寸上收缩,并且干燥过程中样品的表面积没有变化。这限制了溶剂只沿垂直于基板方向蒸发,导致液晶指向器的平面内取向和垂直螺旋轴的产生,因此产生了均匀的周期性螺旋层状结构,具有鲜亮的圆偏振反射色。

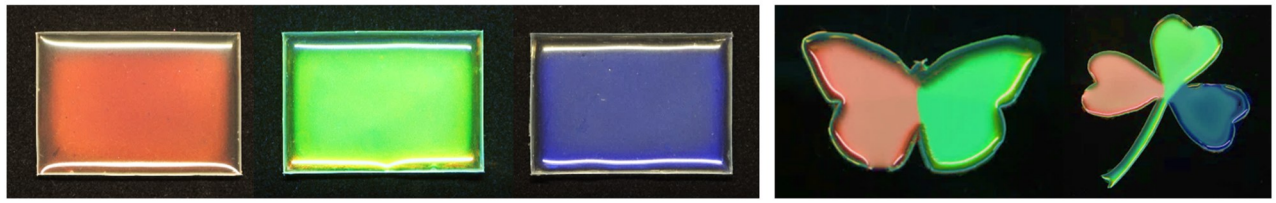
WANG Ling 等^[63]将各向异性挥发方法与巯基-丙烯酸酯迈克尔加成和光聚合反应两步法相结合,制备了具有均匀结构色的 CLCE 光子薄膜。值得一提的是,该制备方法所制备的 CLCE 具有优异的形状及颜色可设计性。例如,将不同的 CLCE 前驱体置于同一基板上,可以制备得到蝴蝶形状和三叶草形状的多色 CLCE 薄膜,如图 5。如图 6(a)所示,在机械拉伸作用下,CLCE 薄膜的颜色能够从红色变为蓝色,且整个过程完全可逆,在机械松弛和颜色恢复之间没有明显的滞后。通过偏光显微镜研究发现,CLCEs 的织构沿拉伸方向变形,并且二维广角 X 射线衍射图由原始的衍射环变为一对衍射弧,表明最初的多畴结构通过拉伸取向变成了单畴结构。作者利用热激活动态 B-O 键交换特性,可以实现对应变诱导的液晶分子排列的固



(a) Molecular structures used for fabricating CLCEs



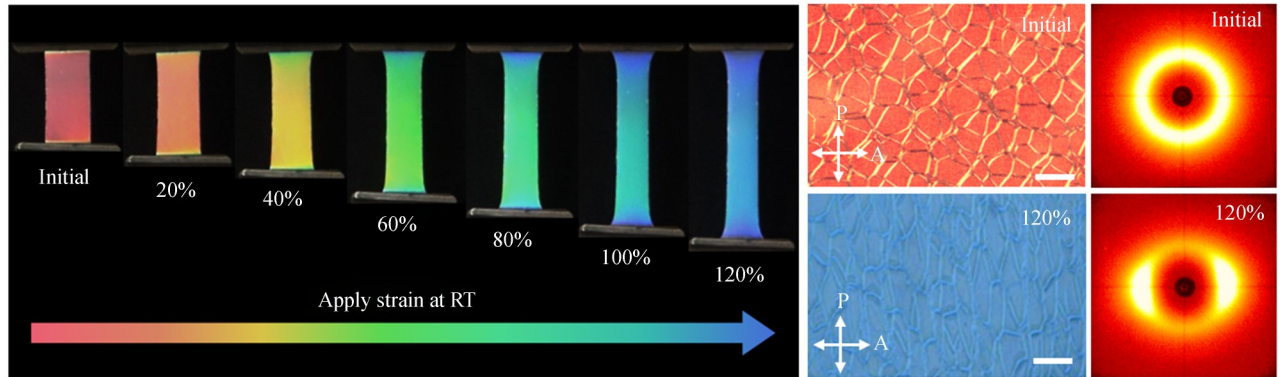
(b) Schematic process of fabricating CLCEs via a facile anisotropic deswelling method that combined two-stage thiol-acrylate Michael addition and photopolymerization reactions



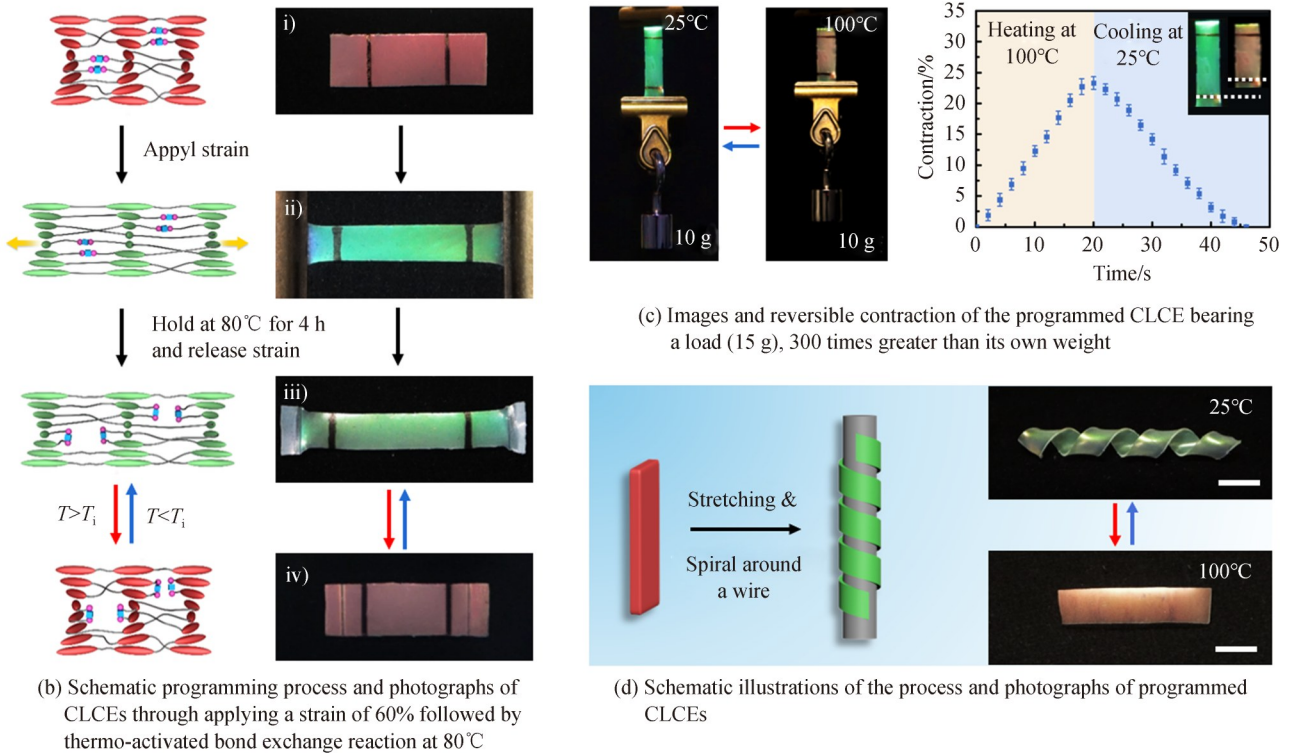
(c) Red, green, blue and multi-colored CLCE films

图5 通过各向异性挥发法制备胆甾相液晶弹性体^[63]

Fig. 5 Preparation of cholesteric liquid crystal elastomers via a facile anisotropic deswelling method^[63]



(a) Photographs of a red-reflecting CLCE film being mechanically stretched (left) and POM image and the corresponding WAXD patterns of the initial and 120% strained CLCE film (right) (scale bar=100 μm)



(b) Schematic programming process and photographs of CLCEs through applying a strain of 60% followed by thermo-activated bond exchange reaction at 80°C

(d) Schematic illustrations of the process and photographs of programmed CLCEs

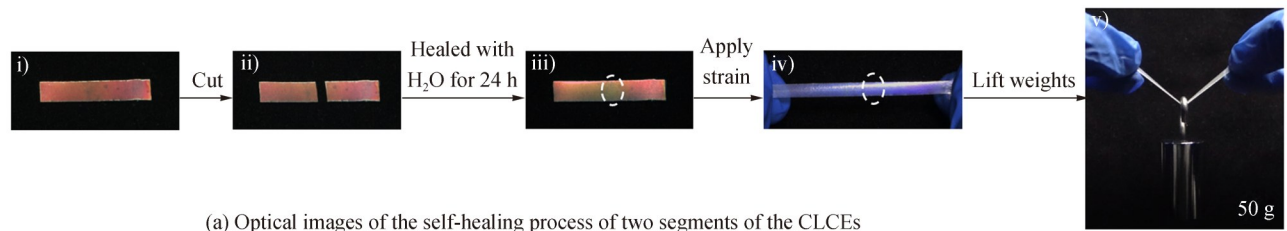
图6 胆甾相液晶弹性体的力致变色及可编程性能^[63]

Fig. 6 Mechanochromism and programmable performance of cholesteric liquid crystal elastomers^[63]

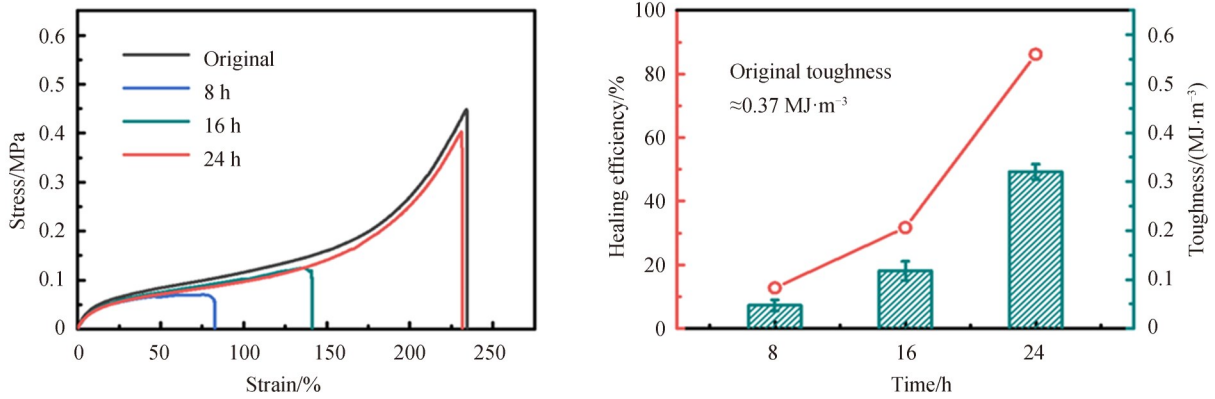
定,从而获得了能够随温度变化实现形状和颜色同时变化的可编程CLCEs。如图6(b)所示,红色CLCE薄膜在室温下单轴拉伸约60%,将拉伸薄膜于80°C条件下(略低于各向同性相转变温度 T_i)放置4h,由于热激活的B-O键交换反应,CLCE聚合物网络形成新的拓扑结构使其保持取向状态。待样品冷却至室温后,可

以得到绿色的 CLCE 薄膜。比较有趣的是,当温度在 25 °C 和 100 °C 之间改变时,CLCE 薄膜在长度和颜色上都呈现可逆变化。取向后的单畴 CLCE 薄膜(~ 50 mg)在 25 °C 和 100 °C 的循环加热和冷却下,可以举起比其自身重量重 300 倍的负载(约 15 g),CLCE 的能量密度(约 20.33 kJ/m³)约为骨骼肌平均能量密度(40 kJ/m³)的一半,如图 6(c)。通过热激活 B-O 键交换还可以将 CLCEs 编程为不同颜色和 3D 形状,如图 6(d)所示,在 100 °C 和 25 °C 的循环加热和冷却下,得到的 4D 光子驱动器不仅可以改变颜色,还可以在 3D 形状和 1D CLCE 薄膜之间可逆变换。

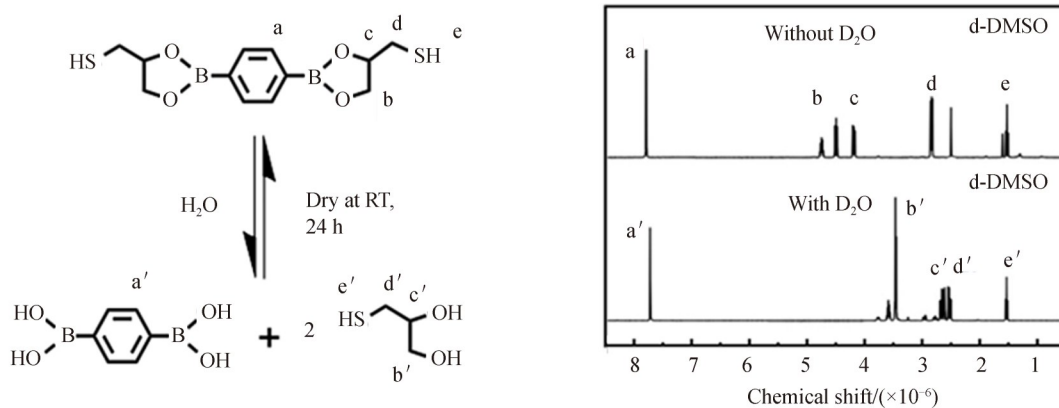
此外,由于动态 B-O 键在水的作用下可以发生断裂/重组,如图 7 所示。作者利用这一特性,将红色的 CLCE 薄膜切成两部分,然后在破损界面上加几滴水,在室温下紧密放置 24 h 后,二者很好地结合在了一起,修复后的样品可拉伸至原始长度的 180%,并且可以举起 50 g 的重量,大约是薄膜本身重量的 1 000 倍。修复



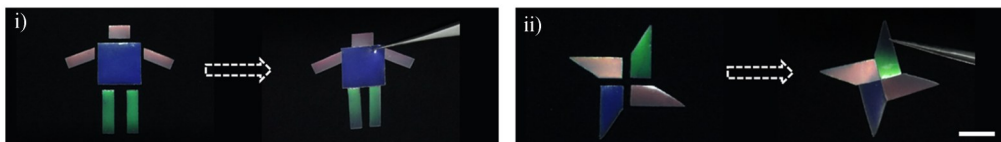
(a) Optical images of the self-healing process of two segments of the CLCEs



(b) Stress-strain curves and self-healing efficiency of self-healed CLCEs at room temperature for a different time



(c) ¹H NMR spectra of BDB in d-DMSO before and after the addition of D₂O



(d) Optical images of a cartoon man pattern and a windmill pattern assembled by the self-healing CLCEs (scale bars=10 mm)

图 7 胆甾相液晶弹性体的自修复^[63]

Fig. 7 Self-healing performance of cholesteric liquid crystal elastomers^[63]

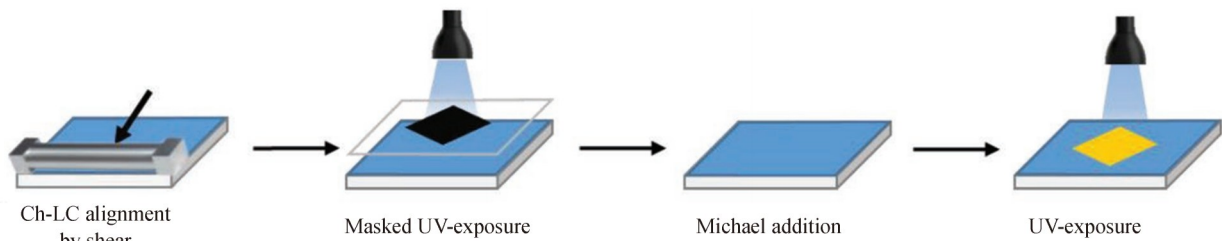
效率定义为恢复韧性与原始韧性的比值,CLCE试样完全切断室温放置24 h后的修复效率约为86.18%。利用CLCEs的自修复性能,作者演示了由不同颜色的CLCEs组装的卡通人物图形和风车图形。该研究提供了一种简便的方法来制备具有机械变色响应、4D(颜色和3D形状)可编程性和高效自修复性能的CLCEs,为4D可编程(颜色和3D形状)光子材料的设计和发展提供全新思路,有望在仿生变色伪装、自适应光学系统和智能机器人等领域获得重要应用。

1.3 刮涂法

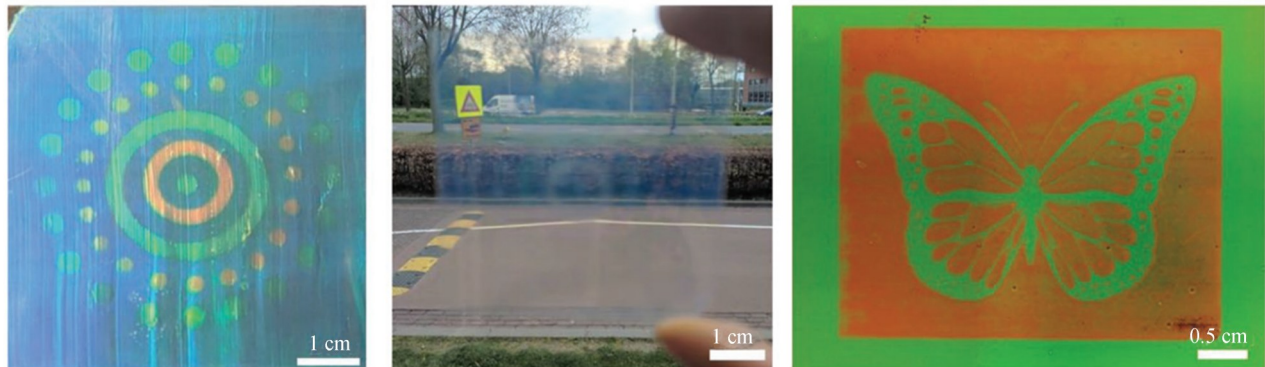
刮涂法^[64-66]是将基板固定在一定温度的热台上,取一定量的液晶前驱体混合物置于刮刀与基底的狭缝处,调节刮刀与基底间的狭缝宽度来调节薄膜厚度,以固定的速度移动刮刀,使前驱体均匀铺满基底,通过光照引发自由基聚合得到交联的胆甾相液晶弹性体薄膜。在刮涂过程中,由于涂布器与基底之间存在剪切力,分子沿着一个共同的方向排列,从而形成了良好的胆甾相螺旋层,在可见光范围内可以观察到明亮的圆偏振反射色,无需额外的取向层。该方法可以应用于双层涂料的制备,以获得反射率接近100%的胆甾相,并制备宽带反射涂料,在不添加额外紫外光吸收剂的情况下,最大限度地减少连续涂层层数。这对于宽带反射光子晶体涂层的大面积制备具有重要意义。

SCHENNING A P H J等^[67]提出了一种利用结构显色法原位监测硫醇-丙烯酸酯迈克尔加成聚合动力学的策略,随着聚合物链增长反应的进行,胆甾相液晶膜的反射光谱发生了红移,可通过凝胶渗透色谱(Gel Permeation Chromatography, GPC)和核磁共振(Nuclear Magnetic Resonance, NMR)分别测定聚合度和转化率。在布拉格反射带移动期间,可以清楚地观察到链长和转化率的增加。经过光聚合交联后,反射带不再发生红移。因此,由于网络的形成,胆甾相液晶反射带可以随时“冻结”。采用该结构显色原位分析方法,交联剂的交联密度和分子量可由迈克尔加成反应时间和单体初始组成来控制。基于此,作者采用刮涂工艺并使用掩膜对单层胆甾相液晶涂层进行阶段性紫外光照,在单层涂层中形成了多色图案,如图8(a)、(b)。通过控制紫外光仅使顶部涂层交联,底部发生聚合物链线性增长,螺距逐渐增大形成梯度结构,在整个涂层厚度上形成一个宽的反射带,使反射波段从120 nm扩大到400 nm。这种原位两步聚合方法提供了一种新的途径来调控光学响应特性,并为制造伪装和防伪材料、宽带红外反射涂层开辟了新的路线。

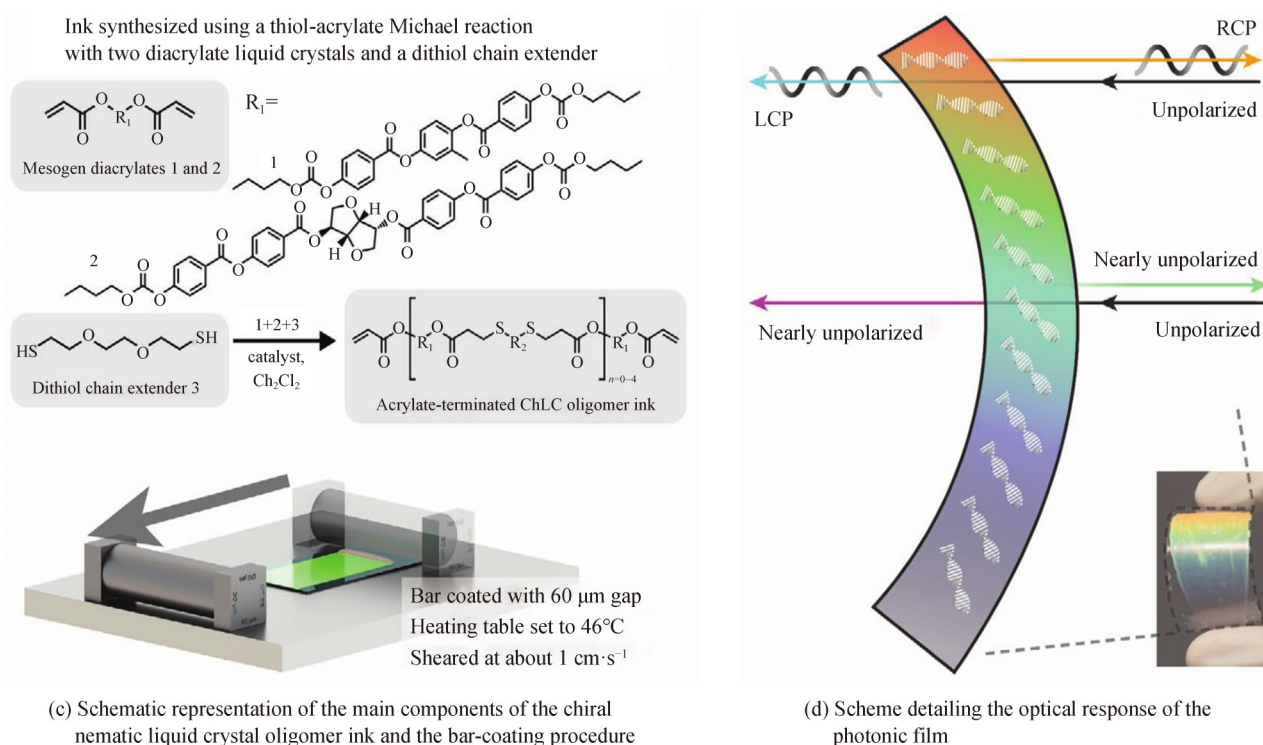
最近,该研究团队采用刮涂法对主链型胆甾相液晶弹性体的圆偏振反射特性进行了进一步的探究^[68]。如图8(c)所示,在刮涂过程中不添加溶剂,而是使液晶低聚物在经过预处理的玻璃基板上融化,研究发现,在46 °C条件下,在胆甾醇中间相进行涂层,可以在几秒内形成一层弹性体薄膜,从而形成大规模的胆甾相液



(a) Schematic representation of the preparation procedure for the patterned photonic coatings



(b) Ch-LC triple pattern formed by dual mask exposure of a single-layered coating and a gravure printed photonic coating showing a Ch-LC green to Ch-LC orange contrast with improved resolution

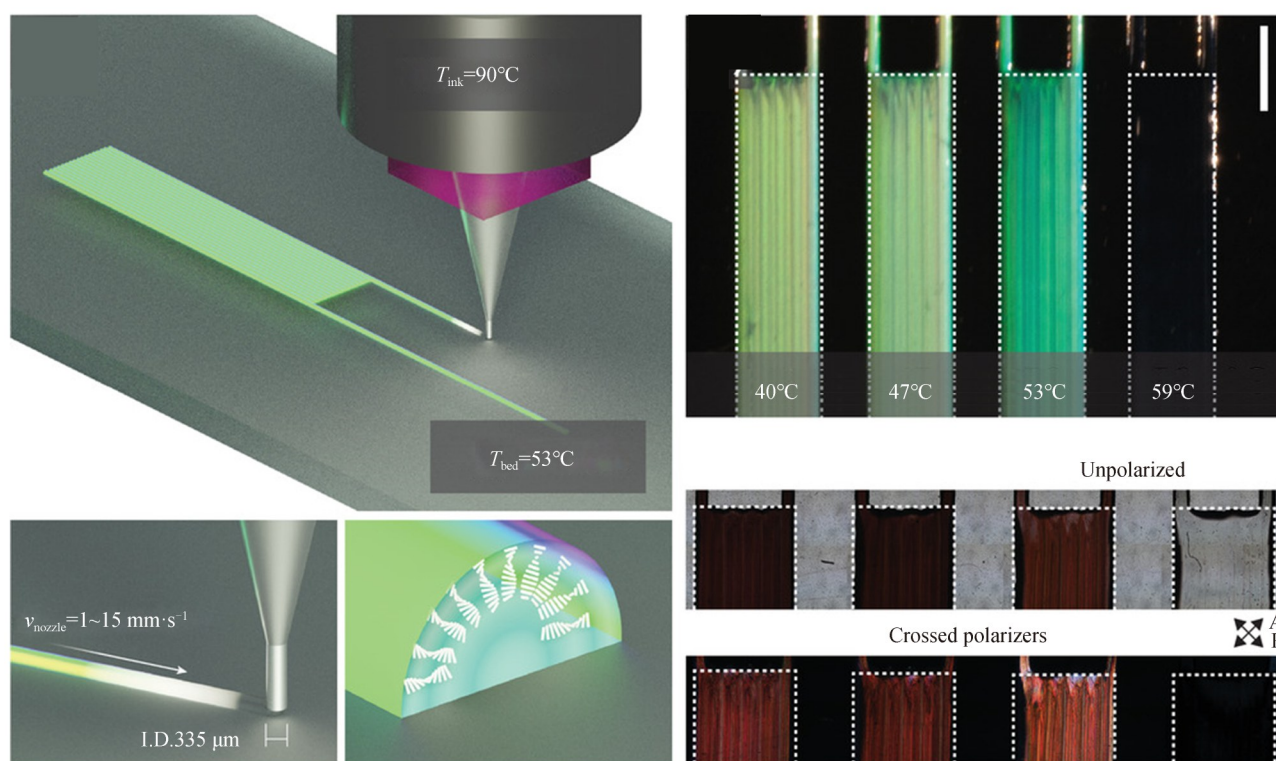
图8 通过刮涂法制备胆甾相液晶弹性体^[67-68]Fig. 8 Preparation of cholesteric liquid crystal elastomers via a bar coating method^[67-68]

晶。采用可角度控制的紫外-可见分光光度法对涂层进行光学表征,结果显示,从表面法线处观察到的反射波长 λ_{max} 并不是预期的那样,相反,从与表面法线夹角大约 50° 的方向观察可以看到明亮的橙色,而从薄膜的另一端看没有显示任何可见的颜色。表明在公式 $\lambda = p \langle n \rangle \cos \theta$ 中 θ 应是和螺旋指向矢 h 的夹角而不是与表面法线的夹角,这主要是由于前驱体的粘度较大导致光轴畸变,形成了倾斜的胆甾相螺旋结构,与使用含有溶剂的前驱体形成的竖直胆甾相结构形成了强烈的对比,如图8(d)所示。作者利用圆偏振滤光片对胆甾相液晶弹性体的圆偏振选择性进行了探究,在垂直于膜表面入射时,常规右旋胆甾相液晶仅反射右旋圆偏振光,而该研究制备的胆甾相液晶弹性体在 λ_{max} 下同时反射了35%~40%的左旋和右旋圆偏振光,不具有圆偏振反射选择性。这种通过剪切和延伸共同作用来对胆甾相螺旋结构进行取向的方式为胆甾相液晶弹性体的3D打印奠定了实验基础。

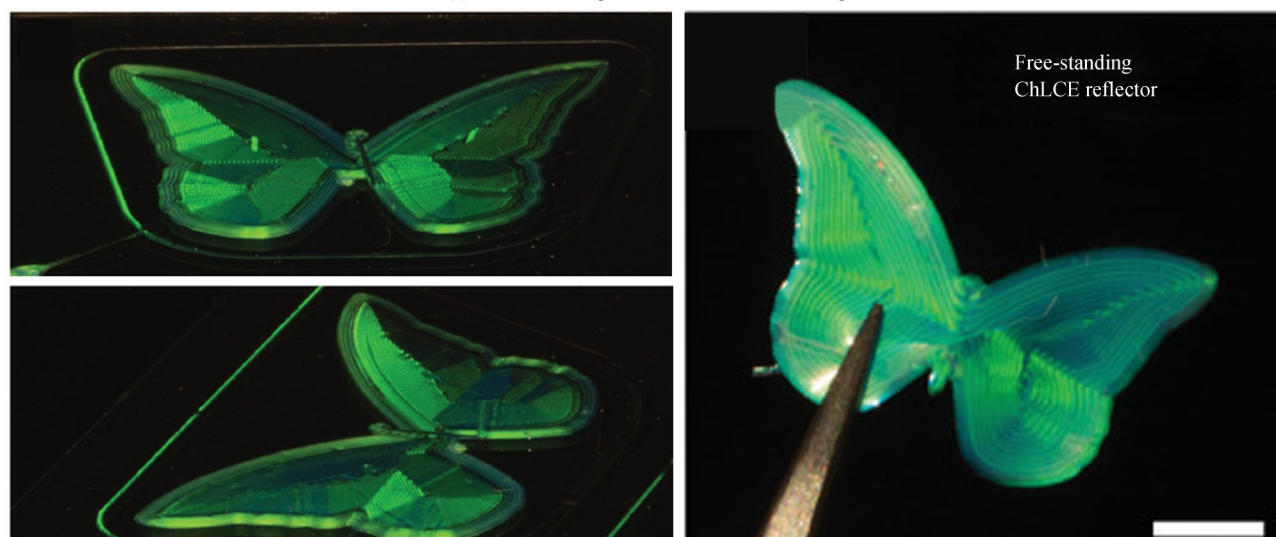
1.4 3D打印法

3D打印作为未来先进制造领域最具发展潜力的技术,其应用已经覆盖组织工程、电子设备和高性能超材料等领域^[69-72]。目前液晶弹性体的3D打印技术包括墨水直写(Direct Ink Writing, DIW)^[73-77]和数字光处理(Digital Light Processing, DLP)^[78-80]。在液晶弹性体的DIW工艺中,由未交联液晶低聚物组成的粘性油墨从打印喷嘴被挤出,在挤出过程中产生的剪切应力使液晶分子自发地沿打印路径排列,形成单畴取向。对于含有手性分子的胆甾相液晶,则形成周期性的层状螺旋结构,选择性地反射圆偏振光。与DIW不同,DLP是一种基于光聚合的工艺,液晶弹性体是通过前驱体混合物的连续薄层光固化来实现的,逐层打印工作效率高,通过这种方式可以创建具有特定复杂结构的3D软体致动器。近年来,科学家们在液晶弹性体的3D打印技术方面取得了重要进展,CAI Shengqiang等^[81]通过控制3D打印液晶弹性体的印刷温度、材料的刚度和收缩能力/致动度,能够通过加热来同时改变同一材料中不同区域的刚度;GE Qi等^[80]通过数字光处理技术实现了液晶弹性体3D打印,用于超轻三维吸能结构的快速成型;LI Shuo等^[79]报道了一种数字光固化方法,液晶低聚物逐层自动剪切取向,以制备具有高能量密度的LCE软体机器人;JENNIFER A L课题组^[82]采用墨水直写技术,制备了以液态金属为核,液晶弹性体为壳的软体致动器,不仅解决了加热单元和液晶弹性体之间力学失配的问题,还可以根据其响应过程中电阻变化实现闭环控制和对外部刺激的感知。

在胆甾相液晶弹性体的3D打印方面,SCHENNING A P H J等^[68]通过对液晶低聚物的直接墨水书写设计制备了主链型胆甾相液晶弹性体,如图9(a)所示。为形成分子螺旋取向,打印是通过温度高于各向同性转变温度的喷头和略低于这个温度的基板来完成的。材料在通过喷嘴时部分冷却,只有当基板保持在53℃或更低的温度时,颜色才会形成;温度越低,颜色越浅,这可能是由于分子排列的有序性降低导致光散射。如果基板高于53℃,则形成各向同性相。在沉积后的几分钟内,用强烈的紫外光照射,使材料充分交联。研究发现,打印速度对螺旋结构的形成也至关重要,在较低的打印速度下,形成了竖直的螺旋轴,随着打印速度的增加,其扭曲程度越来越大,在法向反射的光由单圆偏振转变为几乎偏振无关。研究人员采用不同打印速度制备了一个同时具有偏振选择性和非选择性的蝴蝶形状的胆甾相薄膜,从同一角度看,蝴蝶的边缘



(a) Schematic diagram of the direct ink writing



(b) Butterfly structure observed from different viewing perspectives and free-standing ChLCE reflector

图9 通过墨水直写法制备胆甾相液晶弹性体^[68]

Fig. 9 Preparation of cholesteric liquid crystal elastomers via a direct ink writing method^[68]

和内部还可以反射不同波长的圆偏振光,如图9(b)所示。该研究为用同一种墨水一次性沉积出具有不同光学效果的特殊聚合物光学元件的设计奠定了基础。

2 主链型蓝相液晶弹性体的制备

液晶蓝相通常存在于胆甾相态和各向同性态之间,将手性液晶材料注入液晶盒内,加热到各向同性温度,然后缓慢降温,在一个狭窄温度范围内液晶可以自组装形成三维立方晶格,无需取向层。蓝相液晶体系需要较高手性剂含量,其周期性由晶胞内的晶体排列来定义^[83-86]。2014年,COLES H J等^[87]报道了一项突破性的成果,将软质蓝相材料转化为可拉伸的自支撑蓝相液晶薄膜。在外力的作用下,其应变可以达到原始状态的1.5~2倍,光子带隙随薄膜应变的增加而发生蓝移。在横向拉伸过程中,由于薄膜厚度的减小,沿观察方向有效光子晶格周期性降低,晶格尺度随之减小,如图10(a)和(b)所示。研究者还发现,与未变形的蓝相态不同,机械变形的蓝相液晶表现出普克尔(Pockels)电光效应,其折射率变化与电场强度呈线性相关,

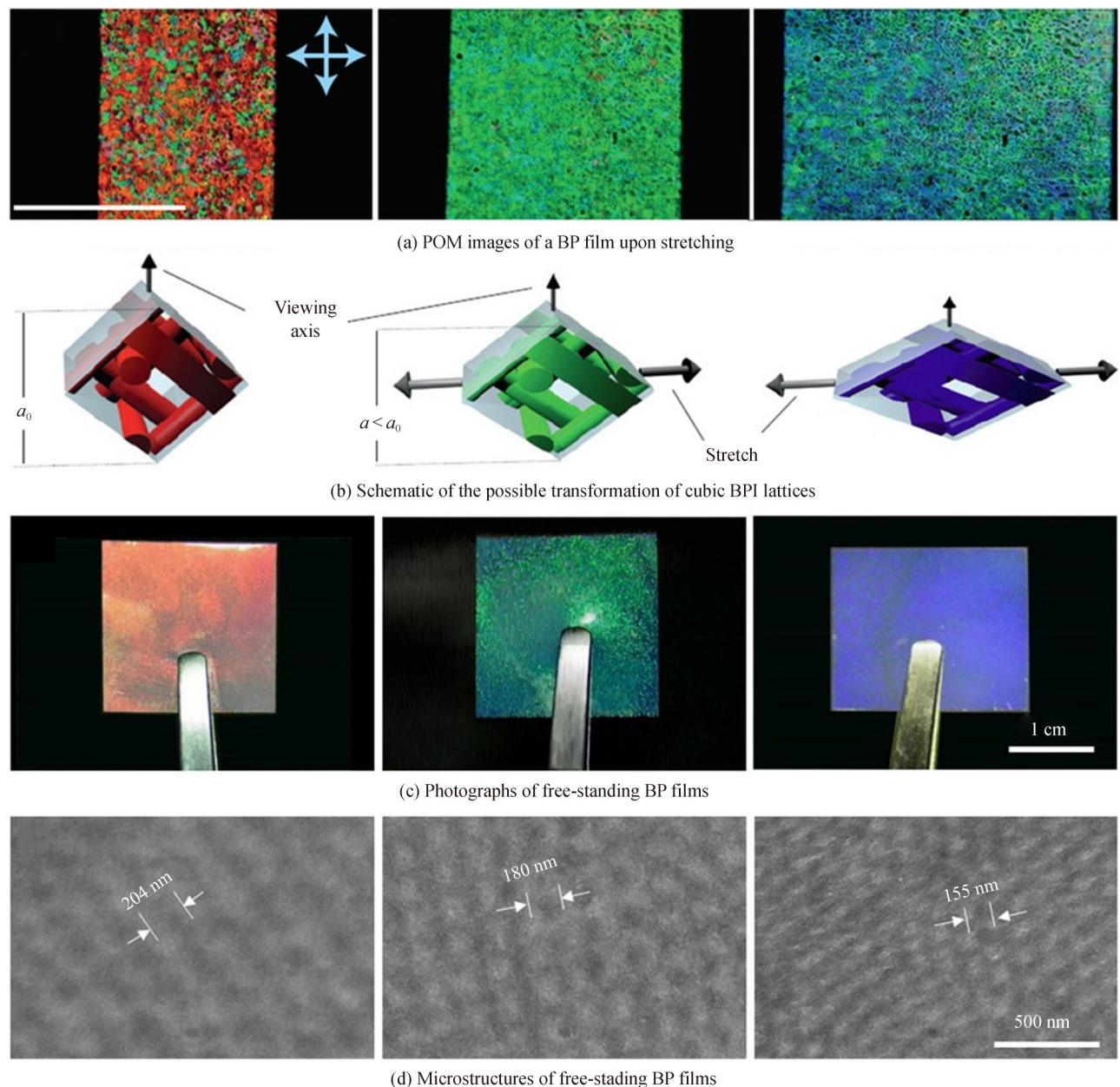


图10 蓝相液晶的结构表征^[87-88]
Fig. 10 Structure characterization of blue phase liquid crystal^[87-88]

这为低压电光器件的发展提供了新的契机。YANG Jiajia等^[88]制备了具有不同结构色的自支撑蓝相液晶膜,如图10(c)和(d),并研究了这种材料的光子形状记忆行为。在不同的机械压力下,通过形状记忆编程实现了多种颜色图案。反射带蓝移是由于蓝相液晶薄膜的压缩变形导致沿观察方向的有效螺距尺寸减小。压缩后的蓝相液晶薄膜在加热到其玻璃化转变温度以上时恢复了原始形状和选择性反射。高效、简便、低成本的蓝相液晶光子材料制备策略不仅可以用于制备光子形状记忆聚合物,还可以用于光学传感器和可重写光子纸。

最近,WHITE T J等^[89]成功制备了一种主链型蓝相液晶弹性体,其先驱体包含丙烯酸酯单体、二硫醇、手性掺杂剂和光引发剂,在自由基光聚合反应前表现出五个液晶相:胆甾相、BPI相、BPII相、BPIII相和各向同性相,并具有较宽的蓝相温度范围,如图11所示。在偏振光学显微镜成像时,蓝相液晶弹性体保留了这些相位的特征双折射纹理,柯赛尔(Kossel)衍射图证实了三维立体晶格的形成。作者探究了机械、热和化学刺激对这种独特的蓝相液晶三维光子晶体的晶格常数和相关光学性质的影响规律。在拉伸过程中,由于折射率周期分布的不对称性,观察到蓝相液晶弹性体从非偏振反射转变为偏振反射,同时由于立方晶格发生畸变,其圆偏振反射色由非角度依赖性变为了角度依赖性。蓝相液晶的晶格周期受温度的影响很小,这是因为BPI和BPII的有效宏观各向同性抑制了与聚合物平均热膨胀系数相关的相对周期性变化的幅度。使用有机溶剂溶胀BPI和BPII液晶弹性体可以产生相当大的颜色变化,偏光显微镜显示选择性反射有明显的红

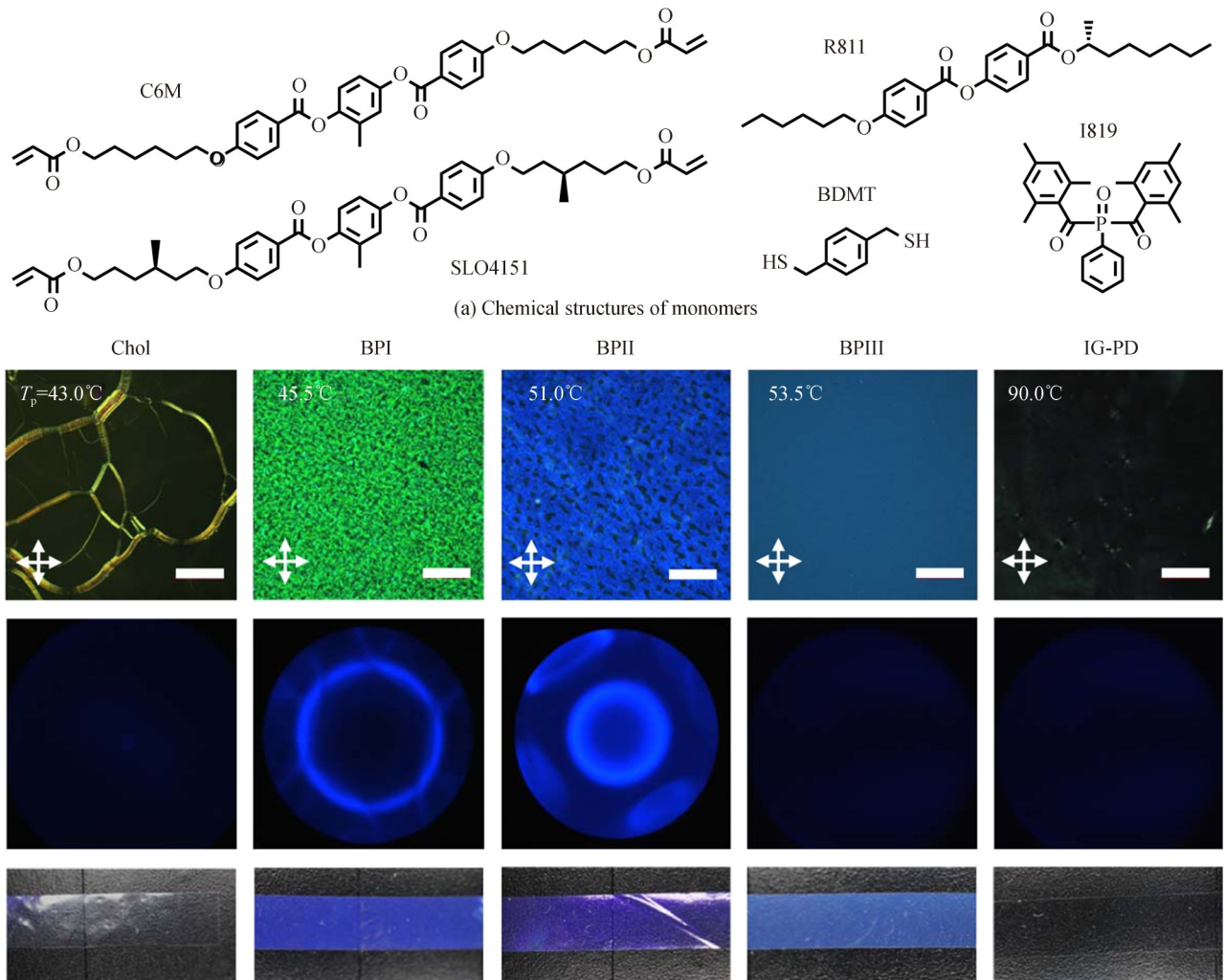


图11 主链型蓝相液晶弹性体^[89]
Fig. 11 Main-chain blue phase liquid crystal elastomers^[89]

移。值得注意的是,这些刺激变形都是可逆的。作为一种轻质、全固态、可变形的光学材料,主链型蓝相液晶弹性体在非线性光学、激光、光谱成像和传感方面具有重要的功能用途。

3 结论

主链型手性液晶弹性体因其独特的圆偏振光选择性反射特性、优异的机械拉伸和可编程性能而受到广泛关注,本文回顾了主链型手性液晶弹性体的研究历史,系统总结了胆甾相液晶弹性体及蓝相液晶弹性体的制备方法。胆甾相液晶主要通过施加外部取向诱导形成周期性螺旋纳米结构,制备胆甾相液晶弹性体的传统方法一般是通过液晶盒的平行取向法,操作简便,结构色均匀,但这种方法的局限在于液晶盒厚度存在一定的限制,通常为50~100 μm 。各向异性挥发法能够大面积制备机械性能优异、高度螺旋取向的胆甾相液晶弹性体,但该方法至少耗时24 h。刮涂法是制备光子涂层的常用方法,通过剪切力进行取向,无需额外的取向层;值得注意的是,当CLCE层做得太厚时,很难得到取向良好的螺旋排列,并且会观察到强烈的光散射。3D打印是一种新兴的制备胆甾相液晶弹性体的方法,大大缩短了材料的制备时间,目前主链型胆甾相液晶弹性体的3D打印仅限于墨水直写法,而数字光处理等3D打印方法可以得到更复杂的三维形状和结构,并且工作效率更高,具有重要的应用价值。蓝相液晶立方晶格的自组装无需取向,在降温过程中自发进行,但这种制备过程常常限于液晶盒内,不利于其大面积制备及商业化应用。因此,研究者还需要探索其他的制备策略来丰富手性液晶弹性体的功能及应用,如利用纺丝技术制备手性液晶弹性体纤维,与金纳米棒、石墨烯、液态金属、Mxene等纳米材料复合赋予其更多的功能。随着材料体系及制备技术的发展,主链型手性液晶弹性体的研究将为仿生学、动态光子学、智能软体机器人和可穿戴设备等的发展提供新的思路。

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Main-chain Chiral Liquid Crystal Elastomers (Invited)

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Abstract: Main chain chiral liquid crystal elastomers, with periodic nanostructures, are a kind of soft photonic crystals, including cholesteric liquid crystal elastomers and blue phase liquid crystal elastomers. They can not only reflect circularly polarized light selectively, but also dynamically adjust their structural color responding to changes in the environment, which could find wide applications in adaptive optics, bionic camouflage, information encryption, intelligent soft robots and so on. With the development of new material systems and advanced preparation techniques, researchers have explored various ways to design and synthesize chiral liquid crystal elastomers for emerging applications. Main-chain cholesteric liquid crystal elastomers are mainly prepared by parallel orientation, anisotropic deswelling, bar coating, and 3D printing. The parallel orientation method is a traditional method, which usually occurs within liquid crystal cells with planar-aligned alignment. Due to the interaction of liquid crystalline molecules with alignment coatings, helical nanostructures' self-assembly can occur. The parallel orientation method has been used to design and develop photonic liquid crystal elastomers, 4D photonic actuators, inflating chiral nematic liquid crystalline elastomers with broadband and pixelated camouflage, chameleon skin-like cholesteric liquid crystal elastomers and other advanced functional materials. Based on the two-stage thiol-acrylate Michael addition and photopolymerization reaction, a facile and easily scalable method has been proposed to prepare uniformly colored large-area cholesteric liquid crystal elastomer films, which benefits from anisotropic deswelling. The gel formation from the Michael addition adheres strongly to the substrate, restricting the deswelling to take place only in the vertical direction and causing an in-plane orientation of the liquid crystal director. The resulted film with helical nanostructures shows a robust, rapid, and reversible mechanochromic response to strain, resulting in a broad color shift across the full visible spectrum. During the bar coating method, the precursor was applied to a bare substrate at a certain temperature via an applicator. Because of the shear forces during the bar coating process, the mesogenic molecules are able to align along with a common director, resulting in the formation of cholesteric liquid crystal elastomers with brilliant reflection color. The thickness of the film was controlled by changing the distance between the applicator and the substrate. This bar coating method has important significance for the application of advanced photonic crystal coatings. 3D printing is an emerging and advanced fabrication technique, and current 3D printing technologies for liquid crystal elastomers include direct ink writing and digital light processing. During the direct ink writing process of cholesteric liquid crystal elastomers, a viscous ink composed of uncrosslinked liquid crystal oligomers is often extruded from the printing nozzle. The shear force generated during the extrusion process causes the mesogens to spontaneously align along with the printing path, forming periodic helical nanostructures that selectively reflect circularly polarized light. Unlike cholesteric liquid crystal elastomers, blue phase liquid crystal elastomers are generally prepared through injecting chiral liquid crystal materials into liquid crystal cells, heating to isotropic phase, and then slowly cooling down. The liquid crystal precursors can self-assemble into a three-dimensional cubic lattice without the assistant of the surface alignment. The resulting blue phase liquid crystal elastomers have narrow photonic band gaps, which could enable functional implementations in nonlinear optics, lasing, spectral imaging and energy applications. In this review, different preparation methods of main-chain chiral liquid crystal elastomers are synthetically introduced. The state-of-the-art advancement and future perspective of main-chain chiral liquid crystal elastomers are discussed. It is expected that this review could shine new light on the development of advanced chiral liquid crystal elastomers and their emerging applications in diverse fields such as adaptive photonics, soft robotics, electronic skins and beyond.

Key words: Chiral liquid crystal elastomer; Main-chain liquid crystals; Photonic crystal; Cholesteric liquid crystal; Blue phase liquid crystal

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