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预聚物对聚合物分散液晶薄膜形貌 及电光性能的影响

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摘要: 聚合物分散液晶(PDLC)作为新型显示材料,简单的制备工艺和较高的性能使其在光电显示领域占据重要地位,受到广泛的关注与研究。构成PDLC的液晶分子与预聚物的种类和含量是调控PDLC微观形貌和电光性能的重要因素。分散在聚合物网络中的液晶微滴尺寸影响着PDLC的驱动电压,而聚合单体的选用则直接影响液晶微滴的大小。本文根据预聚物的不同种类主要综述了(甲基)丙烯酸酯类单体、硫醇/聚硫醇类单体以及常用掺杂剂作为聚合物组成成分时对PDLC微观形貌以及驱动电压和对比度的影响,详细解释了聚合物网络对液晶微滴形貌造成的改变,进而影响电光性能的过程。

关键词: 聚合物分散液晶;预聚物;微观形貌;驱动电压;对比度

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Influence of prepolymer on the morphology and electro-optical properties of polymer dispersed liquid crystal films

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Abstract: Polymer dispersion liquid crystal (PDLC), as a new type of display material, simple preparation process and high performance, make it occupy an important position in the field of optoelectronic display, and has received wide attention and research. The type and content of liquid crystal molecules and prepolymers are crucial to modulate the microscopic morphology and electro-optical properties of PDLC. The size of liquid crystal droplets dispersed in the polymer network affects the driving voltage of PDLC,

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while the selection of polymeric monomers directly affects the size of liquid crystal droplets. The effects of (meth)acrylate monomers, thiol/polythiol monomers, and the common additives as polymer components on the PDLC microscopic morphology as well as the driving voltage and contrast are mainly reviewed in this paper according to the different types of prepolymers. And the process of variation of liquid crystal micro-drop morphology caused by polymer networks, which in turn affects electro-optical properties, is explained in detail.

Key words: polymer dispersion liquid crystal; prepolymer; micromorphology; driving voltage; contrast ratio

1 引言

光电显示器件的出现极大丰富了人们的生活娱乐,但是传统光电器件由于偏振器和取向层的存在导致整体装置复杂,成本较高,成为限制其发展的核心问题^[1-2]。近年来,液晶材料因其独特的介电各向异性和取向有序性被开发运用到光电显示领域^[3],极大简化了显示器件的组件构成和生产成本,其中聚合物分散液晶(PDLC)和聚合物稳定液晶(PSLC)为目前液晶/聚合物复合材料的研究热点。当小分子液晶与预聚物以特定比例共混聚合后,液晶组分的质量分数占总体系40%~60%时,得到PDLC;如果液晶含量提高至90%以上则可以获得PSLC。虽然PSLC中聚合物含量较低,但其聚合后形成的聚合网络会与液晶分子发生相互作用,从而具有保持液晶取向和体系稳定的作用。同时PSLC的双稳态特性和较低的驱动电压令其在反射式显示应用中具有很大的发展潜力,但聚合物含量低使其机械强度较差,并在柔性显示、大面积显示面板方面存在明显缺陷^[4-7]。

PDLC通常是小分子向列相液晶与丙烯酸酯类预聚物在紫外光照下发生相分离所得^[8]。PDLC利用分散在聚合物网络中的微米或纳米级液晶微滴在电关闭和电导通状态下发生取向偏转,从而使液晶的折射率(n_o)与聚合物网络折射率(n_p)相匹配表现出显示性能。当 $n_o \neq n_p$ 时,薄膜呈现不透明状态;当 $n_o = n_p$ 时,薄膜显示透明态^[9-10]。相较于PSLC,PDLC具有良好的成膜能力、稳定的机械性能以及大面积铺设的优点,是柔性显示器件和智能窗口的重要选择材料^[11-12]。同时,PDLC还可以参与制备高介电常数的储能材料,在发挥增塑作用的同时作为电子跳跃的载体^[13]。另外,在PDLC内掺杂

染料和氧化石墨烯可以制备得到具有光响应特性的制动器,响应波长范围可以从可见光延申至近红外光区^[14-16]。除此之外,PDLC在非线性光学材料、传感器、图像集成等领域也具有广泛应用^[17-19]。

通常PDLC在紫外光聚合下的驱动电压较高。在维持紫外光强度、聚合温度、聚合时间等客观环境一定时,液晶和预聚物类型是影响PDLC聚合速率、相分离程度和驱动电压的主要因素^[20-21]。为了获得高效低能的PDLC,预聚物的组分研究成为当下国内外的研究热点。一方面含有刚性的预聚物可以为液晶微滴提供分散空间,同时增强聚合网络的稳定性,而具有柔性链的化合物则保证了聚合反应的进行,二者相辅相成维持了PDLC的稳定性^[22]。聚合网络与液晶微滴的界面相互作用以及预聚物的粘度共同影响聚合物分散液晶薄膜的电光性能和液晶微滴的尺寸^[23]。另一方面不同材料的掺杂和功能基团的作用也在一定程度上调控薄膜的特性^[24-25]。目前依靠上述方法制备的PDLC大多可以达到低于人体安全电压(36 V)的程度,不同的基团和掺杂剂在其中发挥了重要作用^[26-27]。

虽然聚合网络的微观相貌限制了液晶微滴的尺寸和大小,但液晶微滴的形态也受到其内部应力和材料参数等其他因素的影响^[28-31]。由于近年来的研究中采用的液晶材料比较单一,因此本文只针对预聚物对形貌的影响进行介绍,同时综述其对驱动电压和对比度造成的影响。

2 PDLC用丙烯酸酯类预聚物

PDLC用丙烯酸酯类预聚物很容易在光、热、自由基等条件下发生聚合反应,与液晶材料

形成富有柔韧性的薄膜^[32-33]。由于丙烯酸酯易与其他单体发生共聚,因而改变丙烯酸酯衍生物结构可以调控得到不同目标性能的PDLC薄膜。目前丙烯酸酯类预聚物常被分为交联型单体和功能

型单体,预聚物聚合后形成的 n_p 与液晶 n_o 相匹配时,可以得到致密均匀且电光性能优异的PDLC膜,选择合适的预聚物对薄膜的驱动电压和对比度有改进作用。常见单体结构如表1所示。

表 1 常见丙烯酸酯聚合单体结构式

Tab. 1 Common acrylate polymerization monomers

交联型聚合单体		功能型聚合单体	
 butane-1,4-diyl diacrylate BDDA	 2-((acryloyloxy)methyl)-2-ethylpropane-1,3-diyl diacrylate TMPTA	 butyl methacrylate BTMA	 oxiran-2-ylmethyl methacrylate GDMA
 hexane-1,6-diyl diacrylate HDDA	 2,2-bis((acryloyloxy)methyl)propane-1,3-diyl diacrylate PETTA	 2-hydroxypropyl methacrylate HPMA	 (tetrahydrofuran-2-yl)methyl methacrylate THFMA
 decane-1,10-diyl diacrylate DDDA	 2-((3-(acryloyloxy)-2,2-bis((acryloyloxy)methyl)propoxy)methoxy)methyl)-2-(hydroxymethyl)propane-1,3-diyl diacrylate DTTHPA	 2,2,2-trifluoroethyl methacrylate TFEMA	 1-(4-methylcyclohex-3-en-1-yl)ethan-1-ol TOL
 2-(acryloylperoxy)ethyl acrylate PEGDA200, $n=4$ PEGDA400, $n=8-9$ PEGDA600, $n=14$ PEGDA1000, $n=23$		 cyclohexyl methacrylate CHMA	 benzyl methacrylate BZMA

在聚合过程中,交联型单体对聚合物网孔尺寸的形成发挥了重要作用。柔性长链如2-(丙酰氧基)乙基丙烯酸酯除了降低聚合物基质粘度,更重要的是控制相分离过程^[34]。在分子量不变的情况下增加烷基链的长度,反应活性中心减少,预聚物与液晶相分离的动力学过程受到限制,导致反应速率减慢,液晶有充足时间聚集成域,最终扩大了聚合物网络网孔直径,如图1(A)所示。Miki Kshima对PDLC预聚物中短链与长链交联剂的比例进行研究后发现,随着长链交联剂含量的减少,聚合物网孔在逐渐扩大过程中还伴随着从大小不均匀的多孔结构逐渐趋向孔径一致,甚至有聚合物-液晶相分离不均匀的可能^[35]。增加交联剂官能度会减小液晶液滴的尺寸,因为官能度的提高增加了支链结构,预聚物粘度相对长链时有所提高,导致预聚物在相同分子量时的反应点增加,最终使得聚合物网孔减小,如图1(B)^[36]。

交联剂在预聚物体系的占比通常比较小,对

PDLC的微观形态有一定调节作用,更多情况下影响PDLC电光性能的是功能性丙烯酸酯类化合物。通过将极性官能团如羟基(—OH)、氟基(—F)、环氧基等引入丙烯酸酯的端基处改变体系共轭状态或分子间相互作用力,从而可以改变PDLC的电光性能^[37-40]。—OH的氢键作用力与—F的强极性分别使聚合物基质与液晶界面间的作用力即聚合物基质对液晶的锚定能升高与降低。二者同时存在于聚合物基质中时,—OH造成的膜附着力提高了PDLC的对比度和驱动电压,而—F由于降低了预聚物对液晶的粘度使PDLC的驱动电压降低,所以当聚合达到饱和之后,产生了低驱动电压与高对比度的聚合物分散液晶材料。这与不含羟基和氟基的组成相比,电压降低了约40%,对比度提高了约50%^[38]。

甲基丙烯酸酯衍生物由于其强稳定性逐渐在预聚物中变得不可缺少,但是向其中引入刚性基团增加了聚合物的粘度,不仅对驱动电压有影响,还降低了PDLC膜的关态透过率(T_o),进而

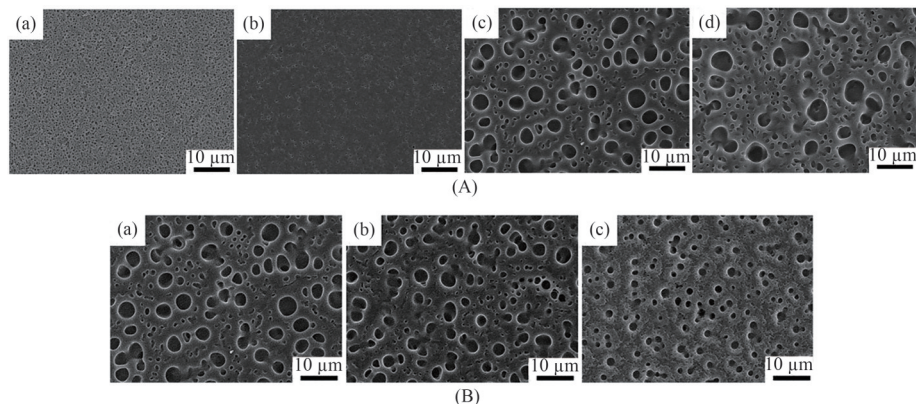


图1 (A)不同交联剂链长的PDLC薄膜形态的显微照片。(a) PEGDA200, (b) PEGDA400, (c) PEGDA 600, (d) PEGDA1000; (B)不同官能度的丙烯酸酯交联剂的PDLC薄膜的形态的显微照片。(a) TPMTA, (b) PETTA, (c) DTTHPA^[36]。

Fig. 1 (A) Microphotography of morphology of PDLC films with different crosslinker chain length. (a) PEGDA200, (b) PEGDA400, (c) PEGDA 600, (d) PEGDA1000; (B) Microphotography of morphology of PDLC films with different functionality of acrylate crosslinkers. (a) TPMTA, (b) PETTA, (c) DTTHPA^[36]。

提高了对比度^[41]。这一点与—OH的引入提高聚合物薄膜的对比度方式是一致的。不同结构端基的引入对PDLC的驱动电压和对比度都有着显著影响^[42],端基在聚合反应中都存在相应的作用方式,因此组合适当的预聚物化学结构可以有效避免重复实验与原料浪费。杨槐课题组曾对PDLC采用的液晶含量和不同单体结构、含量以及微观形貌影响电光性能做了详细的研究^[37-38, 41]。最近Mohsin Hassan Saeed研发了一种A3DA-PDLC,可以获得 $0.55 \text{ V}/\mu\text{m}$ 的阈值电压(V_{th})(同比下降75%)和16.82的对比度,如图2。普通PDLC的聚合物网孔在缩小时驱动电压增加,但A3DA-PDLC在因网孔减小导致液晶散射中心增加,对比度升高的同时可以保持驱动电压的下降,这得益于A3DA与液晶化学结构的相似度提高了彼此的相容性,这对未来构建新型丙烯酸酯单体提供了新的思路^[43]。

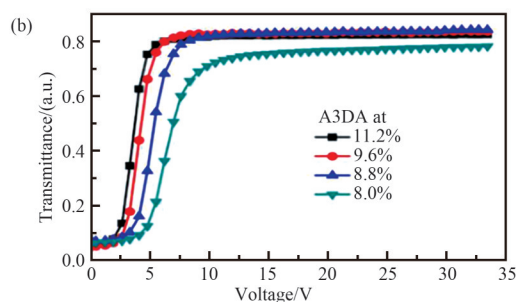
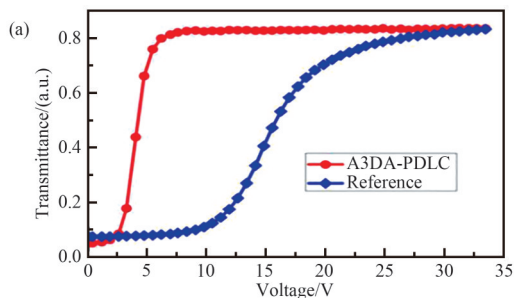


图2 (a)含9.6%和0%(质量分数)A3DA的PDLC的V-T图;(b)含有不同A3DA浓度的PDLC的V-T图(303 K, $\lambda=633 \text{ nm}$)^[43]。

Fig. 2 (a) Transmittance dependence on the applied electric field for A3DA-PDLC (mass fraction 9.6% A3DA) and reference cell (0% A3DA) measured at 303 K, $\lambda=633 \text{ nm}$; (b) Voltage-transmittance (V-T) curves for PDLCs prepared with A3DA at different concentrations at 303 K, $\lambda=633 \text{ nm}$ ^[43]。

3 PDLC添加硫醇/聚硫醇类预聚物

PDLC薄膜的聚合物网络在形成过程中存在预聚物与液晶材料的扩散竞争。当液晶扩散速率低于预聚物时,液晶微滴分散不及时,最终导致网络尺寸过小或相分离不完全。Yi Zhang于2017年报道了硫醇化合物的掺入对聚合物基体形貌和聚合物分散液晶电光性能的影响,指出硫醇预聚物的引入造成了硫醇-丙烯酸酯反应和



丙烯酸酯聚合反应的竞争。前者生成线性聚合物,后者为网络形态。硫醇-丙烯酸酯反应生成独特的微球形貌,在不同的反应速率下分别形成致密网络、附着微球的网络、带有小网络的大网孔。特别是当硫醇含量过高会使聚合网络消失,由此也得出交联剂对聚合网络形成具有不可替代的作用^[44-45]。最近,有研究指出在保持外界环

境不变的情况下,将硫醇多面体低聚硅氧烷(POSS-SH)与预聚物混合可以有效调控 PDLC 网络的形貌与电光性能。一方面原因是 POSS-SH 降低了聚合物的表面能;另一方面则是 POSS 的微观笼状结构会产生液晶分子与聚合物表面的斥力作用。POSS-SH 的化学结构与测试聚合物表面能方法如图 3 所示^[46-48]。

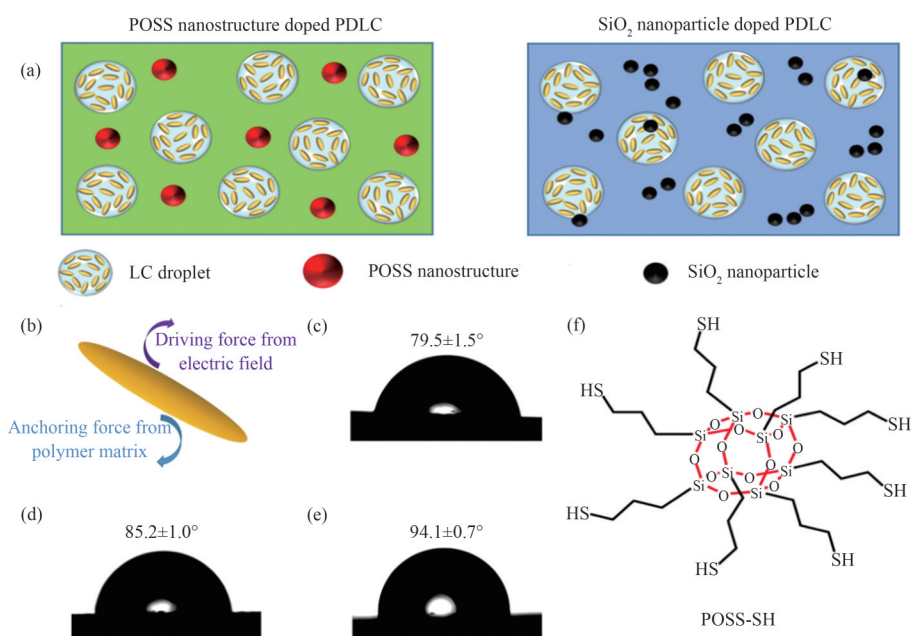


图 3 (a)PDLC 内部硅纳米结构分布的示意图;(b)电场下 PDLC 样品中液晶分子的受力情况示意图;使用蒸馏水图像对含有不同 POSS-SH 质量分数的聚合物进行接触角测量:(c)0%, (d)4% 和 (e)8%;(f)POSS-SH 的化学结构^[48]。

Fig. 3 (a) Schematic diagram of the distribution of silicon nanostructure inside the PDLC; (b) Schematic of the force condition on the LC molecule in a PDLC sample under an electric field; Contact angle measurements using distilled water images of the polymers containing different POSS-SH content (mass fraction): (c) 0%, (d) 4% and (e) 8%; (f) Chemical structures of the POSS-SH^[48].

不同官能度的硫醇预聚物与交联剂、液晶材料混合时,硫醇官能度越多的预聚会因较高的交联度而形成分子链更致密的有序排列。Ying Li 将 TTMP(3SH)掺杂在预聚物中进行紫外聚合获得了均匀的微观层状结构,进一步提高官能度(PETMP, 4SH)后形成更为规律的鳞片结构,这是分子排列更为紧密的表现^[49]。在硫醇化合物不超过丙烯酸酯预聚物整体含量的 1/2 时,硫醇基对最终 PDLC 薄膜的饱和电压(V_{sat})起降低作用。虽然添加硫醇单体可以一定程度上降低 PDLC 驱动电压,但是 T_0 因比表面积提高而大幅降低了对比度^[50]。因此预聚物中添加硫醇单体可以得到无刺激气味、不易与空气发生作用的惰性 PDLC 薄

膜,更加适合投入产业化应用。

4 PDLC 掺杂其他物质

驱动电压和对比度是聚合物分散液晶最重要的电光性能。Ag、Au、TiO₂、CeO₂、CuO、BaTiO₃ 等纳米颗粒掺杂到 PDLC 中产生的主体-客体相互作用可以有效增强界面极化,改变聚合物网络的形貌,最终达到优化电光性能的目的^[51-55]。除此之外,染料分子、多壁碳纳米管等材料掺杂到 PDLC 中也得到了充分的研究。图 4 为掺杂染料分子的 PDLC 的微观结构图。如果分别将质量分数为 1%、3%、5% 的偶氮染料甲基红(MR)掺

杂在向列相液晶 E63(25%)与 NOA65(75%)聚合物中,MR与聚合物基质几乎不存在相容性,但在液晶相中可以达到较好的分散效果。这是因为二色性偶氮染料分子的长轴倾向于在向列相液晶中沿液晶的指向矢排列。因此当入射光的偏振光平行于液晶长分子轴时,大部分能量被同方向排列的染料吸收,导致聚合物基质的聚合速率降低,最终影响 PDLC 的网孔和液晶微滴的大小^[56]。同样当染料 3-[N-乙基-4-(4-硝基苯偶氮)苯氨基]丙腈添加到液晶 HPC850100-100 和 NOA65 混合物中时,也可以得到染料在低掺杂时含量越高,聚合网孔越大,整体网络相对均匀分布的结果,同时在染料含量为 0.007% 时得到了最佳薄膜。此时染料掺杂聚合物分散液晶(DPDLC)的 CR(241)、 V_{th} (0.85 V/ μm)和 V_{sat} (1.45 V/ μm)是最优结果,比没有任何掺杂的 PDLC 驱动电压都要低^[57]。

染料分子较高的二色性比和高阶参数表现出与向列相液晶相似的棒状结构,多壁碳纳米管(MWCNT)也因其化学结构与液晶中的苯环产生 π - π 相互作用而可以少量地分散在液晶相中形成碳纳米管掺杂的聚合物分散液晶(CPDLC)。如图 4(b)所示,无电场时掺杂在聚合物中的 MWCNT 随机取向,通电后表现部分取向的特性。它的分散对聚合物网孔并没有明显影响,但是 MWCNT 的偶极性质可以在电导通状态时降低介质的电阻率、提高电容,从而降低 CPDLC 的驱动电压($V_{MWCNT(0\text{ mg})} = 60\text{ V}$ 、 $V_{MWCNT(0.03\text{ mg})} = 30\text{ V}$)^[58]。Yourong Liu 进一步以外加电场转折点的频率推断出多壁碳纳米管在液晶区域和聚合物区域的质量分布,表明 MWCNT 一半集中在液晶区域^[59]。另外量子点也可以作为一种掺杂剂改变其电光性能,但其主要针对介电性能的改善拓宽了 PDLC 在激光、传感器领域的应用^[26,60]。

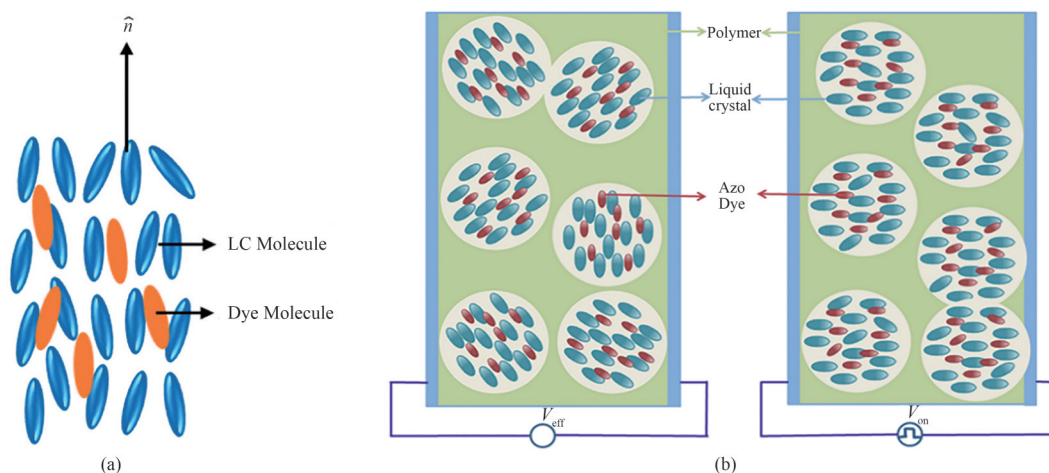


图4 (a)混合物中染料分子与液晶分子的取向示意图;(b)掺杂MR染料的PDLC在通电前后液晶微滴的变化^[56-57]。

Fig. 4 (a) Schematic diagram of the orientation of the dye and liquid crystal in the mixture; (b) MR doped PDLC cell^[56-57].

5 结论与展望

本文主要介绍预聚物对聚合物分散液晶微观形貌和电光性能影响的国内外研究进展,主要针对(甲基)丙烯酸酯型、硫醇型化合物以及掺杂剂对PDLC的影响进行综述。PDLC的驱动电压和对比度是其作为显示材料的重要参数,同时预聚物的微观形貌直接影响其电光性能的优劣。聚合分散液晶的聚合单体和液晶材料能够在光诱导下

发生相分离行为,液晶微滴由此以微米或纳米级尺寸分散在聚合物当中形成独特的聚合网络。致密均匀的网络依靠不同单体的合适配比形成,整个聚合过程中单体所含功能性基团如—OH、—SH、液晶材料、外界环境以及掺杂物质等都对PDLC有着重要影响。PDLC与染料、量子点等功能材料的结合拓宽了液晶在激光传感、柔性显示等领域的应用,因此了解混合物组成结构的进展对进一步优化其电光性能和应用领域具有重要意义。

当前单纯围绕降低 PDLC 驱动电压的工作已经逐渐不能满足社会需要的发展。设法将 PDLC 的柔性功能、简单易制等优势与其他领域相结合可以拓宽 PDLC 的应用范围,最大化获得普适性更强的高效低能的器件。另外,虽然通过实验结果可以得出不同组合单体聚合成 PDLC

的形貌和性能,但如果能够研发出基于单体结构预测聚合物分散液晶薄膜形貌及性能的计算机模拟系统,则可以大幅节约资源,提高 PDLC 调制效率,降低成本。因此,在聚合物分散液晶单体聚合过程中,聚合结果模拟和电光性能计算预测也将会成为未来重要的研究方向之一。

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