分子凝胶的拓展研究: 有序三维荧光传感薄膜和低密度多孔材料的创新制备

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摘要 经过几十年的发展, 分子凝胶研究取得了巨大的进步. 然而, 这些研究大多还停留在开发新的胶凝剂、发现新的凝胶体系和揭示新的胶凝机理. 在未来的研究中, 如何更好地发挥分子凝胶的优势, 推进分子凝胶的现实应用已经成为该领域研究人员的共同期盼. 考虑到: (1) 有序或部分有序小分子胶凝剂三维网络结构的形成是分子凝胶赖以存在的基础, (2) 内相多孔网状结构的存在有助于荧光敏感薄膜材料获得良好传感性能, (3) 凝胶乳液的液-液两相特点有可能因凝胶作用的发生而转化为固-固(凝胶-凝胶)或固-液(凝胶-液)两相结构等因素, 在过去的10年里, 作者实验室将分子凝胶策略引入到新型荧光敏感薄膜材料、凝胶乳液和以凝胶乳液为模板的低密度多孔材料制备中, 由此, 获得了一系列性能优异的敏感薄膜材料和油水分离材料, 拓展了分子凝胶研究. 本文结合本课题组工作实际, 阐述分子凝胶策略在功能界面材料制备中的应用, 提出分子凝胶拓展研究面临的主要挑战, 展望分子凝胶拓展研究的前景和发展趋势.

关键词 小分子胶凝剂, 分子凝胶, 凝胶乳液, 荧光薄膜, 低密度多孔材料

自20世纪90年代初以来, 分子凝胶研究持续发展, 迄今为止见诸报道的小分子胶凝剂已经达到上万种^[1]. 特别是随着超分子化学和纳米科技的飞速发展, 人们对分子凝胶的研究视角日益多样, 理解也更加深入透彻. 同时, 通过实验研究和计算机模拟的结合, 分子胶凝理论逐渐成型, 相应的分子凝胶制备也从多年前的偶然性发现逐渐过渡到有目的的设计阶段^[2~4]. 不同于其他领域的化学研究, 分子凝胶研究具有突出的跨学科性质. 一般而言, 分子凝胶研究起码要包含软物质、自组装、流变学、热力学、合成化学、理论计算和模拟等^[1].

在宏观上, 分子凝胶具有类固体性质. 从微观上

看, 分子凝胶是少量小分子胶凝剂通过分子间弱相互作用形成的三维网络结构将大量溶剂经由毛细作用、表面张力等固定化的结果^[5]. 因此, 分子凝胶具有典型的微多相结构特征. 此外, 分子凝胶组成的小分子特点和凝胶形成的超分子作用特征使得分子凝胶在性质上既不同于化学凝胶, 也不同于基于高分子化合物的物理凝胶, 具有更加突出的热可逆性、剪切触变性和其他重要的刺激响应性^[1~4]. 这些性质是分子凝胶获得特殊应用的基础, 然而, 令人遗憾的是, 迄今为止, 有影响的分子凝胶大规模应用还未见到报道.

影响分子凝胶现实应用的一个重要因素就是分

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子凝胶的稳定性^[1]。这是由于分子凝胶的形成和存在是建立在多种弱相互作用之上的一种溶解-聚集平衡态,外界任何微小的刺激都有可能打破这种平衡,从而引起分子凝胶的融化相变^[6]。这就使得要获得长期稳定的分子凝胶就必须设法强化维持溶解-聚集平衡的因素。例如,采用高沸点液体,借以防止溶剂挥发所引起的凝胶-溶胶相变。通过封装实现隔热减振,从而克服振动、受热等因素引起的凝胶破坏等。事实上,就是以这样的思路实现了基于分子凝胶的智能推进剂的制备。

推进分子凝胶实际应用的另外一种思路是将其作为一种介质,构建结构特殊性能优异的特别材料,从而彰显分子凝胶的应用价值。正是按照这一思路,在过去的几年里,作者实验室成功地将分子凝胶应用于荧光敏感薄膜材料、凝胶乳液和以凝胶乳液为模板的低密度多孔材料的制备,获得了一系列性能优异的功能表界面材料,展示了分子凝胶的研究意义和应用价值。本文结合本课题组工作实际,阐述分子凝胶策略在三维荧光传感薄膜材料和低密度多孔材料制备中的应用(图1)。在此基础上,提出相关研究面临的主要挑战,展望分子凝胶拓展研究的前

景和发展趋势。

1 分子凝胶策略在高性能荧光传感薄膜创制中的应用

相对于均相(溶液)化学传感器,薄膜传感器具有不污染待测体系、可重复使用、易于器件化等优点,因而备受人们青睐。其中,以荧光为传感信号的薄膜化学传感器更有灵敏度高、检测信号丰富、不消耗试剂、无需参考物,甚至可实现远程检测等优点,近几十年来得到了迅猛发展^[7~11]。然而,薄膜基荧光传感器的研制基础是高性能荧光敏感薄膜材料。换言之,创制性能优异的荧光传感薄膜在发展高性能荧光传感器过程中具有基础性作用。荧光薄膜的传感性能决定于薄膜的组成和结构。一般而言,可以通过灵敏度、选择性、响应速度、可逆性、重现性和薄膜的化学稳定性等衡量薄膜的传感性能。因此,恰当选择传感单元和薄膜制备方法是获得理想荧光传感薄膜的根本,提高单位面积中有效传感位点数目是构建性能优异荧光传感薄膜的主要途径^[10]。众所周知,组成分子凝胶的主要成分是溶剂,通过胶凝剂分子超分子聚集形成的凝胶网状结构仅占总质量的2%

图1 以所制备荧光传感薄膜为核心部件开发的两款不同型号的便携式爆炸物探测仪(a), (b), 荧光薄膜放大制备设备(c), 分子凝胶策略制备的柔性和耐低温低密度多孔材料(d), (e)和材料的内相显微结构(f)~(h)。 (i)所示为利用分子凝胶策略制备有序三维荧光传感薄膜和低密度多孔材料的基本策略

Figure 1 Two portable detectors (a) and (b) for explosives detection with fluorescent sensing films as the core part. (c) The equipment for fabrication of fluorescent sensing film in large scale. (d), (e) Some flexible low temperature resistant low density porous materials and their corresponding internal structures (f)~(h). (i) shows the basic strategy in fabricating self-assembled fluorescent sensing films and low density porous materials through molecular gel strategy

左右^[12~14]。因此,以恰当方式除去溶剂所得到的干凝胶应该具有多孔网状结构特征,这种分子水平上的良好通透性对于提高薄膜传感的响应速度、改善薄膜传感的可逆性,乃至薄膜中荧光活性传感单元的光化学稳定性都具有十分重要的意义。此外,良好的分子凝胶往往还具有剪切触变性,这就为通过喷涂、旋涂获得均匀薄膜提供了方便。基于这些考虑,提出将荧光活性单元引入小分子胶凝剂中,通过分子凝胶策略,获得荧光活性分子凝胶,再以其为介质构建具有三维网状结构特点的荧光薄膜材料,以期大幅度改善传统荧光薄膜的传感性能和制备过程的可重复性。

与经由普通旋涂、浸涂、流延等物理过程所得到的无序物理薄膜和经过固液界面化学反应所得到的有序单层化学薄膜相比较,基于分子凝胶策略所得到的薄膜在本质上属于物理薄膜,在结构上具有化学薄膜的有序或部分有序性。这就使得这类薄膜不但具有常规物理薄膜所具有的制备方便、易于放大,基质易于再生获得重复使用等优点,而且也拥有单层化学薄膜所具有的结构均匀、传质阻力小、薄膜响应速度快、可逆性好等特点。与此同时,规避了单层化学薄膜荧光活性单元面密度小、制备困难、难以放大制备等问题,为荧光传感薄膜材料的稳定高效制备奠定了基础。基于此,制备了一系列有序三维荧光传感薄膜材料,实现了对氨气、氯化氢、苯胺、化学毒剂和冰毒及冰毒类似物的高灵敏和选择性检测^[14~21]。

1.1 有序三维荧光传感薄膜的分子设计

合适的胶凝剂分子是构建有序三维荧光传感薄膜的基础,因此,荧光分子的设计、合成至关重要。一般而言,这类荧光胶凝剂分子需要满足两个基本要求:(1)所选荧光基团对特定待测物具有一定的响应。目前已报道的荧光分子种类繁多,结构不同,因此,对不同对象表现出不同的响应行为。例如,茈萘酰亚胺衍生物多属于缺电子化合物,在条件合适时,其荧光会被一些能级匹配的负电子化合物猝灭;茈萘的单体荧光和激基缔合物荧光截然不同,某些环境因素的变化会引起两种结构之间的转化,从而实现对环境因素改变的监测;7-硝基苯并-2-氧杂-1,3-二唑衍生物易与氨类化合物发生作用而引起荧光强度的变化,由此可以设计氨类化合物荧光传感器。(2)所选结构应该包含能够促进凝胶形成的结构片段。经

过几十年的发展,人们已经发现长链烷烃、胆甾类、脲基、糖类、氨基酸及多肽、脂肪酸等结构的引入有助于分子凝胶的形成,因此,在设计荧光胶凝剂时,往往要根据最终薄膜的使用环境要求,引入某些特定结构片段,以期通过分子凝胶策略,得到高性能荧光传感薄膜材料。为此,在过去的几年里,我们将三联噻吩、茈萘酰亚胺、茈萘、7-硝基苯并-2-氧杂-1,3-二唑等荧光单元与胆固醇、葡萄糖、氨基酸等典型的小分子胶凝剂结构片段组合,获得了一系列具有自组装性能的荧光分子。通过研究所获荧光活性胶凝剂分子在不同溶剂中的胶凝行为和流变学性质,选择合适凝胶体系进行旋涂、喷涂转移,制备具有良好通透性的荧光薄膜材料^[15~22]。在此基础上,深入研究所获薄膜的光物理性能和传感行为,筛选能够满足实际工作要求的薄膜制备传感器件。这些研究不仅拓宽了分子凝胶的应用范围,更为新的高性能荧光传感薄膜的制备奠定了坚实的基础,从而推动了荧光传感薄膜的创制研究。

1.2 用于气相检测的有序三维荧光传感薄膜

胺类(包括氨和有机胺)污染物是重要环境污染物,是威胁人类健康的一类重要化学物质^[23]。同时,包括毒品在内的许多禁用药品的成分也是有机胺类物质或其类似物^[24]。因此,开发高灵敏、高选择性氨和有机胺类化合物传感器具有重要的意义。茈萘酰亚胺是一种化学稳定性好、量子产率高、光电性能优越的荧光活性化合物,其衍生物在液晶和有机光电材料制备,在特殊超分子结构搭建等方面获得了广泛应用^[25]。值得关注的是,通过辅助基团的引入可以大幅度改变茈萘酰亚胺的最高占据轨道(HOMO)和最低空轨道(LUMO)能级,从而使其与特定胺类物质的轨道能级相匹配,促进胺类与茈萘酰亚胺衍生物光激发态间的电子转移,实现对胺类的特异性检测^[26]。此外,胆固醇具有强烈的形成超分子有序结构的趋势^[14],将其与茈萘酰亚胺结合,有望获得新型荧光活性小分子胶凝剂,从而为有序三维网状荧光敏感薄膜的制备打下基础。

基于上述考虑,设计、合成了化合物1~3(图2)^[15~17],研究了各化合物在不同溶剂中自组装行为,考察了不同结构薄膜的传感性能。结果显示,薄膜的传感性能强烈依赖于其微观结构,简单旋涂所获薄膜的传感性能远不及通过分子凝胶策略所制备的薄膜。观

图2 (网络版彩色)化合物1~3的分子结构及其形成的自组装结构

Figure 2 (Color online) Structure of compound 1~3 and their self-assembled structured in film state

察图2可以看出,利用分子凝胶策略构建的薄膜具有明显的网状结构.具体来讲,薄膜1由直径约为80 nm的纤维构成(图2(a))^[15];薄膜2以直径约为150 nm的球状堆积结构为特征(图2(b))^[16];薄膜3则由直径约为100 nm的纤维堆积而成(图2(c))^[17].这些薄膜在有机胺检测中表现出良好的传感灵敏度、响应速度和传感可逆性.此外,如同预期的一样,薄膜也拥有良好的光化学稳定性.当然,由于组成和结构的差异,三种薄膜的传感性能又有所不同:常见有机胺几乎均可猝灭薄膜1的荧光,猝灭效率介于60%~80%^[15];薄膜2对这些有机胺也敏感,但猝灭效率介于40%~85%^[16];薄膜3则对甲基苯丙胺等表现出特殊的响应性,检出限低至5.5 ppb^[17].造成这些差异的根本原因是花酰亚胺结构中的修饰片段不同,从而导致其HOMO和LUMO能级不同、自组装结构不同^[15~17].

7-硝基苯并-2-氧杂-1,3-二唑(NBD)是生物成像和分析中的常用试剂,具有荧光量子产率高、对环境变化敏感等特点^[26].本课题组^[18,27,28]首次将其引入小分子胶凝剂,获得了一系列具有良好机械强度、自愈合性质和传感性能的小分子凝胶.例如,将NBD经由苯丙氨酸与胆固醇连接,获得的化合物4(图3)^[18]可以胶凝二甲亚砜(DMSO),该凝胶对氨气表现出很好的可逆刺激响应性:氨气的引入引起凝胶向溶胶的快速转变,并伴随体系荧光的猝灭;通入氮气或空气

驱除氨气,溶胶立即重新恢复为凝胶态,体系荧光也随之恢复(图4(a)~(d)).有意思的是,凝胶的微观形貌可以通过胶凝剂的浓度来调节,随着胶凝剂浓度增大,胶凝剂聚集结构逐渐由松散相对无序的纤维转变为有序的纤维阵列(图3(c)~(g)),为构建高性能传感薄膜奠定了基础.基于这些研究结果,经过喷涂或高速旋涂制备了荧光薄膜材料(薄膜4),经过进一步

图3 (网络版彩色)化合物4的分子结构(a和b)及其在DMSO中形成的干凝胶的扫描电子显微镜(SEM)照片.(c)~(g)不同浓度的化合物4在DMSO中形成的干凝胶的SEM照片.图中所示标尺为3 μm

Figure 3 (Color online) Structure of compound 4 (a) and (b) as well as the xerogels (c)~(g) obtained from different concentration of the compound in DMSO. Scale bar: 3 μm

图4 (网络版彩色)化合物4的DMSO凝胶对氨气的可逆响应(a)~(d). (a)和(b)是自然光下化合物4的DMSO凝胶在通入氨气前后的照片; (c)和(d)分别是(a)和(b)在紫外灯下的照片. (e)和(f)所示为以化合物4的DMSO凝胶制备的荧光传感薄膜为核心部件构建的荧光传感器件应用于监测氨气泄漏: (e) 无氨气泄露; (f) 有氨气泄露

Figure 4 (Color online) Fluorescence response of the DMSO gel of compound 4 to ammonia (a)–(d). (a) and (b) are the DMSO gel of compound 4 before injection of ammonia in sunlight; (c) and (d) are the corresponding pictures of (a) and (b) under UV light, (e) and (f) show the device containing fluorescent sensing film by using DMSO gel of compound 4 for monitoring ammonia leaking ((e) without ammonia leaking; (f) ammonia leaking)

的器件化, 获得了可用于监测氨气泄漏的氨气荧光化学传感器(图4(e)~(f)). 这一工作展示了有序三维荧光薄膜的传感应用前景, 彰显了分子凝胶在构建网状有序结构中的巨大价值.

氯化氢是一种对人类健康危害极大的刺激性气体. 在近地太空, 氯化氢的存在还会极大地影响正常的大气过程, 从而影响人类赖以生存的地球环境, 因此, 气相氯化氢的灵敏检测意义重大^[29]. 几年前, 本课题组^[19]设计合成了一种具有双极性结构特点, 头尾均为葡萄糖、侧链为胆固醇的1,4-双(取代苯乙炔基)苯取代物(化合物5, 图5(a)). 在氯仿中, 该化合物以球状聚集体存在, 将其转移至玻璃基质表面可得到均匀的荧光薄膜. 薄膜的表面性质(亲疏水性)可通过采用不同的干燥方式进行控制: 快速干燥得到疏

水薄膜; 缓慢干燥得到亲水薄膜(图5(a)). 依此得到了两种具有不同微观形貌的三维荧光薄膜. 其中一种由直径约为1~3 μm 的球状颗粒组成(薄膜5); 另一种由直径约为10 μm 的囊泡构成(薄膜6). 传感实验表明, 两种薄膜对气相氯化氢响应差别极大, 薄膜5对氯化氢存在十分敏感, 且响应可逆(检测限: $\sim 0.4 \text{ ppb}$ ($10^{-9} n_{\text{HCl}}/n_{\text{空气}}$))(图5(b)), 而薄膜6对氯化氢的存在并不敏感, 88~2860 ppm ($10^{-6} n_{\text{HCl}}/n_{\text{空气}}$)的高浓度氯化氢也仅能猝灭其荧光强度的25%(图5(c)). 这一研究表明可以通过引入性质不同的辅助基团调节荧光基团的组装行为和性能. 此外, 薄膜5和6对氯化氢气体传感性能的巨大差异证明了微观组装结构对薄膜传感性能的巨大作用, 也进一步说明组装技术在传感薄膜制备中的重要作用.

图5 (网络版彩色)(a) 化合物5的分子结构以及利用其制备荧光传感薄膜的示意图; (b), (c) 薄膜5和6对氯化氢气体的荧光响应曲线. 从图中可以看出, 薄膜5的响应性能明显要优于薄膜6

Figure 5 (Color online) Structure of compound 5 and fabrication of compound 5-based fluorescent sensing film (a). Fluorescence response of film 5 (b) and film 6 (c) to HCl and it is obvious that film 5 performs much better than film 6 in HCl sensing

1.3 液相检测用有序三维荧光传感薄膜

水体污染一直是困扰人类的一大难题, 发展水体有毒有害化学品便捷、可靠检测方法具有重要的意义. 与气相检测用有序三维荧光传感薄膜制备过程相类似, 本课题组^[20~22]设计合成了一系列具有自组装性能的荧光小分子化合物, 利用分子凝胶策略制备了一系列有序三维荧光薄膜. 通过光物理性质和传感性能研究, 实现了对神经毒素、有机磷农药、甲醛等的可视化检测. 此外, 这些方法多数不但灵敏度高, 选择性也很好, 有些甚至可以进行器件化, 实现重复使用, 具体内容可参见文献^[20~22].

2 分子凝胶策略在凝胶乳液和低密度多孔材料制备中的应用

由于密度小、孔隙率高、比表面积大、孔径可控等优点, 低密度多孔材料在分离、催化、传感器、分子识别、生物组织工程以及环境科学等领域得到越来越

越广泛的作用^[30~32]. 多孔材料制备的关键是孔径大小、形状和分布调控, 以及孔表面的功能化^[33]. 目前, 常用的多孔材料制备方法主要包括气体发泡法、溶剂致孔法和模板法等^[34]. 相对于发泡法和溶剂致孔法, 模板法由于具有易于精确控制孔洞大小和分布等优点而备受青睐. 凝胶乳液是制备低密度多孔材料的常见模板. 凝胶乳液(gel-emulsions)也称之为高浓乳液(highly concentrated emulsions)、高内相比乳液(high internal-phase ratio emulsions)^[35]. 表面上, 凝胶乳液与普通凝胶没有区别, 但在内部结构上, 凝胶乳液完全不同于这些凝胶. 微观上, 凝胶乳液由两个性质完全不同的物相组成. 其一为连续相, 其二为分散相. 此外, 与普通乳液也不同, 作为反应介质, 凝胶乳液具有一系列突出的优点^[35~38]. 例如: (1) 亲水亲油区域同在使其可以同时溶解极性相反的两种或两类反应物; (2) 两相之间界面巨大, 反应物碰撞机会多, 反应效率高; (3) 体系的黏弹性使反应产物不易析出, 有助于网状聚集结构的形成; (4) 以油包水(W/O)

型凝胶乳液为反应介质时,水占据主要部分,因此可以大幅度减少有机溶剂排放,有助于保护环境,降低成本;(5)产品大小和形状很容易以模具控制;(6)产品的多孔结构可以通过改变凝胶乳液的组成进行控制.作为反应介质,凝胶乳液还可以兼备模板和溶剂等多重作用,因此,被广泛用于低密度多孔材料制备.

稳定剂的应用是凝胶乳液得以存在的关键.到目前为止,已知的凝胶乳液稳定剂主要是普通表面活性剂、微纳米颗粒材料(包括有机和无机)以及近期由作者团队率先提出的小分子胶凝剂等^[38~51].以小分子胶凝剂作为稳定剂的凝胶乳液,稳定剂用量一般不超过连续相(多为有机相)的3%(w/v),远远低于以表面活性剂为稳定剂的常见凝胶乳液中稳定剂的用量^[38,44~52].相对于以微纳米颗粒材料为稳定剂的凝胶乳液,基于小分子胶凝剂的凝胶乳液稳定性要好得多,几乎完全避免了相反转等微纳米颗粒材料基凝胶乳液常常遇到的问题.此外,基于小分子胶凝剂的凝胶乳液,分散相体积分数也不受74%下限的限制,两相体积比可以在更大范围内调控,这就使得凝胶乳液模板法制备的多孔材料内相结构更加丰富.更为重要的是,稳定剂用量少使得最终材料的分离纯化变得简单,成本也得以控制.基于这些考虑,在过去的几年里,本课题组^[47~52]将分子凝胶策略用于新型凝胶乳液制备和低密度多孔材料的模板合成,获得了一系列性能优异的低密度多孔材料,探索了其在吸附分离方面的应用.

2.1 用于浮油分离的低密度多孔材料

随着现代化水平的不断提升,石油开采、炼制和

应用日益广泛,随之而来的石油和石油炼制品泄漏问题也不断出现,给环境生态和人类健康带来了极大的威胁^[53,54].高效吸收是控制石油和石油炼制品泄漏危害的有效手段,但这一措施的实施有赖于高效吸附材料应用.因此,发展低成本高效石油和石油制品吸收材料具有重要的意义.多孔材料是最为常见的高效吸收材料,材料的组成、结构、疏水疏油性、机械性能和稳定性等决定着材料的使用性能,而材料的成本和制备过程的复杂性决定着材料能否获得实际应用.为此,几年来,本课题组^[47~52,55]通过新型小分子胶凝剂创制,得到了一系列以可聚合单体或可缩合反应前驱体为连续相,组成结构各异的凝胶乳液,以其为模板制备了多种低密度多孔材料,实现了对石油、石油制品,特别是环境有害有机溶剂的温和高效吸收分离.

早在2008年,本课题组^[45]就设计合成了双胆固醇衍生物**6**(图6),实现了对正庚烷、正辛烷、正壬烷、正癸烷、煤油、柴油、汽油等多种有机溶剂的室温高效胶凝,并首次获得了以小分子胶凝剂为稳定剂的油包水(W/O)型凝胶乳液.研究表明,该凝胶乳液具有良好的稳定性和典型的泡沫结构.

同年,又制备了基于胆固醇二茂铁衍生物的多重刺激响应性分子凝胶^[14],之后又发展了更多的胆固醇二茂铁衍生物型小分子胶凝剂.值得关注的是,以化合物**7**(图6)为稳定剂^[48],可以制备一系列W/O型凝胶乳液.当选用甲基丙烯酸叔丁酯为连续相,通过改变体系组成和对其进行引发聚合,获得了一系列聚合物多孔材料(图7).该材料可用于有机溶剂的高效吸收,且通过挤压有机溶剂得以回收,材料因之可以获得重复使用,此过程可重复至少13次(图8).研

图6 化合物6~9的分子结构

Figure 6 Structure of compound 6~9

图7 (网络版彩色)化合物7形成的油包水型凝胶乳液(a)以及聚合所得块材的照片(b)和SEM照片(c). 凝胶乳液的连续相(油)主要成分为甲基丙烯酸叔丁酯

Figure 7 (Color online) W/O gel-emulsion based on compound 7 (a) and the corresponding monolith obtained by polymerization of the gel-emulsion (c). The continuous phase (oil) of the W/O gel-emulsion is tert-butyl methacrylate

究还表明,在连续相引入反应性硅烷化试剂能够显著改善材料的机械性能和吸附性能.

2013年,本课题组^[49]以含双醇羟基的新型胆固醇衍生物(化合物8,图6)为稳定剂,得到了新的W/O型凝胶乳液,以其为模板,制备了超低密度多孔聚苯乙烯块材.材料制备工艺简单,条件温和,无须超临界、冷冻等高耗能干燥过程,也不需要溶剂置换等高成本后续处理过程.在应用方面,该材料可选择性高效去除水体中的少量有机溶剂,经过简单挤压、洗涤

和干燥,材料就可获得重复使用(图9).

之后,本课题组^[50]又合成了以苯丙氨酸为连接臂、羧基为末端的胆固醇衍生物(化合物9,图6),该化合物是很好的凝胶乳液稳定剂.经过配方优化,有机无机复合等途径,得到了兼顾机械强度和柔韧性的低密度多孔材料,在材料密度为 0.18 g/m^3 时,压缩量达70%时,材料形状依然可以完全恢复,压缩循环25次后材料各项性能依然没有明显改变(图10),为实际应用奠定了坚实的基础.

2.2 用于VOCs吸附的低密度多孔材料

空气污染的高效治理是人类面临的一大难题,尤其是挥发性有机物(volatile organic compounds, VOCs)的治理更具挑战性^[56,57].事实上,空气中的VOCs清除已经引起了世界各国政府的高度重视.吸附法由于具有安全、方便和经济可行等优点,在VOCs治理方面获得了重要应用^[58,59].基于凝胶乳液法在多孔材料制备方面的优势,作者实验室设计合成了含有不饱和双键的胆固醇衍生物(化合物10,图11(a)),以其为稳定剂制备了多种以可聚合单体苯乙烯为连续相的W/O型凝胶乳液,通过引发聚合获得了多孔材

图8 (网络版彩色)(a)基于化合物7制备所得块材对不同有机溶剂的最大吸附量; (b)不同块材对煤油吸附过程的可逆性测试; (c)制备所得的较大块材照片

Figure 8 (Color online) Maximum oil adsorption capacities of the monolith (obtained by using compound 7 as the stabilizer) to nine different liquids (a); the reversibility of the absorption processes (kerosene as an example oil) (b) and a photo of a typical monolith (c)

图9 (网络版彩色)以化合物8为稳定剂所制备多孔块材在(汽)油水分离中的应用。(a) 在水中加入染色汽油;(b) 将块材浸入油水混合体系;(c) 吸收汽油后的多孔块材;(d) 分离块材;(e) 回收块材和汽油;(f) 清洗块材,干燥后重复使用

Figure 9 (Color online) Application of the monolith (obtained by using compound 8 as stabilizer) in water/oil separation. (a) Gasoline polluted water (a fluorophore was used to dye the gasoline), (b) the monolith was used to absorb the gasoline, (c) all of the gasoline was successfully absorbed, (d) the oil-filled monolith was removed from the water, (e) most of the gasoline was squeezed out, and (f) residual gasoline was washed out by a drop of organic solvent, and the monolith could be reused after natural drying in air

图10 (网络版彩色)以化合物9为稳定剂所得多孔块材的可逆压缩性能。(a) 块材的应力-应变曲线;(b) 压缩变形的回复性能;(c) 块材压缩回复照片
Figure 10 (Color online) (a) Compressive stress-strain curves of the monolith (obtained by using compound 9 as the stabilizer) compressed to 50% strain; (b) the monolith along the compression axis during cyclic compression to 50% of its original size (note: the compression was repeated 25 times, and the scaffold regains its original size after each compression); (c) sequential photographs of the compression test illustrating spring-back behavior

图 11 (网络版彩色)化合物 10 的分子结构(a)以及所获块材(b). (c) 多孔块材对BTEX(苯、甲苯、乙基苯、对二甲苯)的吸附性能; (d) 常温常压下, 多孔块材对甲苯吸附量的时间依赖性

Figure 11 (Color online) Structure of compound 10 (a) and a photo of the obtained monolith (b); (c) adsorption capacities of the monolith to BTEX (benzene, Toluene, ethylbenzene and *p*-xylene); (d) adsorption capacity of the materials to toluene (T) as a function of time

料(图11(b))^[51]. 实验表明, 该材料对苯、甲苯、乙基苯以及二甲苯(BTEX)等常见VOCs具有突出的吸附能力, 有望在环境VOCs清除方面获得应用(图11(c)和(d)).

3 结论与展望

物理凝胶, 特别是小分子化合物和溶剂组成的分子凝胶是传统化学合成技术和当代超分子化学组装技术综合运用所创造的重要物质形态. 与化学凝胶不同, 分子凝胶中的网络结构依靠胶凝剂-胶凝剂分子之间氢键、 π - π 堆积、疏水相互作用、静电相互作用、偶极相互作用等弱键相互作用维系. 这种结构上的差异使得化学凝胶和分子凝胶在受到外场作用时会表现出完全不同的性质. 例如, 在搅拌、泵送、晃动等剪切作用下, 两类凝胶虽然都可因为其中网络结构的破坏而发生相分离或相转变, 但就化学凝胶而言, 这种破坏一旦发生, 就不能逆转, 而分子凝胶则有可能因剪切作用的去除而发生相态逆转. 正是分子凝胶所具有的这种刺激响应性使其在模板合成、控制释放、组织培养、温和分离、信息储存与感知等方面表现出巨大的应用前景. 除了刺激响应性之外, 分子凝胶还具有胶凝剂含量低等特点. 这就使得以其为介质, 研究分子识别、进行化学转化、发展分子材料、实现结晶纯化具有其他介质无法比拟的优势. 从这个观点来看, 将分子凝胶研究拓展至高性能

荧光敏感薄膜制备、凝胶乳液制备和低密度多孔材料的模板合成只是分子凝胶研究的初步拓展. 相信未来的研究领域将会更加广阔、研究的内容将会更加丰富. 就目前可以预期的深化研究而言, 可以在以下几个方面做出尝试: (1) 液-液萃取技术的革新. 将分子凝胶引入传统液-液萃取将会极大地促进液-液萃取技术的发展, 这是由于分子凝胶一般都具有剪切刺激相变性质, 使得由凝胶-液体构成的萃取体系在振荡下会以液-液形式工作, 表现出与普通液-液萃取一样的效率, 而在静置后, 体系转化为凝胶-液体体系, 本来的液-液分离因此而转化为固-液分离. 由此可见, 基于分子凝胶的液-液萃取将有可能兼有液-液萃取的高效性和固-液分离的方便性; (2) 高品质晶体的获得. 溶剂是分子凝胶的主体成分, 且分子凝胶可因需要而转化为液体. 这种特性使得以分子凝胶为结晶介质时, 在不妨碍晶体的分离收集条件下, 可以有效防止器壁对晶体生长的不利影响, 因而, 有望在高品质晶体制备中获得应用; (3) 固液悬浮体系的稳定化. 固液混合体系的储存固态化, 使用流动化是众多工业过程的现实需求, 分子凝胶策略的运用有可能很好地满足这两个看似相互矛盾的要求, 从而解决与之相关的一系列问题. 当然, 已经获得的分子凝胶应用也存在研究继续深化的问题. 例如, 以分子凝胶策略得到的荧光薄膜材料就存在基质表面黏附性不

高、易于脱落等问题,要使相关薄膜获得规模应用,就必须解决这些问题.此外,以小分子胶凝剂为稳定剂的凝胶乳液模板法制备低密度多孔材料的工作也有待进一步的发展,如何获得力学性能更加优异,内

相结构更加丰富,甚至具备超材料性质的低密度多孔材料需要尽快提到议事日程.不过,毫无疑问,经过几十年的积累,分子凝胶研究已经面临一个从基础研究走向高技术应用的巨大机遇.

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Summary for “分子凝胶的拓展研究：有序三维荧光传感薄膜和低密度多孔材料的创新制备”

Extended research on molecular gels: From the perspective of development of three dimensional fluorescent sensing films and low-density porous materials

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Low molecular-mass gelators (LMMGs) were first reported in the 1930s, but interest in the field was dwindled for several decades until the mid-1990s when Shinkai, Weiss and their colleagues re-started the research in the field based on newly developed supramolecular principles. Since then, remarkable progress has been achieved on LMMGs-based molecular gel research. However, most studies till now have been focused on the design of new LMMGs, discovery of new gels, and reveal of new gelation mechanisms. As pointed out by Weiss in one of his recent reviews (*J Am Chem Soc*, 2014, 136: 7519–7530), few applications of molecular gels have been realized as of yet. The reasons behind partially are their limited lifetimes and mechanical strengths at ambient conditions. Therefore, in future studies, the way to make molecular gels work into their advantages and promote their practical applications will be highly concerned.

With consideration of the following characteristics of molecular gels, fluorescent films for sensing, and gel-emulsions based on LMMGs: (1) presence of three dimensional (3D) networked structures is a pre-requirement for molecular gel formation, (2) increasing porosity is beneficial for enhancing the sensing performance of fluorescent films, and (3) the internal structures of gel-emulsions would change from liquid-liquid to liquid-solid (liquid-gel) or even solid-solid (gel-gel) after gelation of one or both of the continuous and dispersed phases of the systems which may be induced by introduction of LMMGs, we introduced molecular gel strategy in fabrication of smart fluorescent sensing films and creation of new kind of gel-emulsions as well as the relevant low-density porous materials.

It is known that the structure of a gel could be tuned by variation of the structure and concentration of the gelator used in the system. The gel structure is also dependent upon the nature of the solvent or solvent mixtures. These facts suggest that molecular gel structures could be largely tuned via different ways. Moreover, the molecular gel structures, which is in fact the self-assembled structures of the gelators within the gels, are generally ordered, at least partially ordered, due to competition of crystallization and dissolution during the gelation process, laying foundation for specific applications. Generally, the amount of gelator in a molecular gel accounts for only 2% (w/v) around, which means the main component of a gel is solvent. Therefore, evaporation of solvent produces networked porous xerogels, implying that porous and highly, at least partially, ordered films could be fabricated via a physical coating technique with the molecular gels as coating materials, which is the so called molecular gel strategy. The key point in the fabrication of high-performance fluorescence sensing films via the molecular gel strategy is design of fluorescent LMMGs. Through comprehensive study of the photophysical properties, the gel formation behaviors of the fluorescent gelators, fluorescent films with preferable adlayer structure could be obtained. In this way, a variety of fluorescent sensing films with 3D porous and networked structures have been developed in the authors' laboratory during the last few years. The analytes studied include mainly aniline, ammonia, hydrogen chloride, nitro-aromatics, some organophosphorus pesticides, nerve agents, formaldehyde, and some illegal drugs, etc.

As for gel-emulsions, stabilizer is the most important component in the systems. For conventional gel-emulsions, the stabilizers used are generally surfactants and micro/nano particles. Nearly ten years ago, we introduced LMMGs as a new kind of stabilizers. Unlike surfactants and micro-/nano-particles, the amount of LMMGs used in gel-emulsions is much less, which normally accounts less than 4% (w/v) of the continuous phase. The LMMGs-based gel-emulsions have better stability and several sticky problems encountered in conventional gel-emulsions have been avoided. In addition, the volume fraction of dispersed phase in the LMMGs-based gel-emulsions is not restricted by 74%, which is the minimum volume fraction of dispersed phase for surfactants or micro-/nano-particles based gel-emulsions. In other words, with introduction of LMMGs as stabilizers, the internal structures of gel-emulsions could be tuned in a much wider range, which is favorable for template preparation of porous polymeric materials. Importantly, less stabilizer consumption is favorable for cost saving and makes separation and purification of the final materials much easier. Based upon these considerations, LMMGs-based gel-emulsions have been employed for preparation of low density porous monoliths. The materials as obtained show remarkable adsorption of organic liquids both in condensed and gaseous phases. Moreover, the materials can also be used for absorption of oil (organic liquids) from immiscible oil-water mixtures.

In this review paper, we elaborate the application of molecular gel strategy in developing functional surface and interface materials based on the work conducted in our group. We will summarize the challenges in further research related to molecular gels and make prospect on the future study on this important area of science.

low molecular-mass gelators, molecular gels, gel-emulsions, fluorescent films, low-density polymeric monoliths

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