智能高分子开关膜的制备方法研究进展

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[摘要]　智能高分子开关膜是将智能高分子与非刺激响应型基材膜结合而成。由于智能高分子能够响应外界刺激发生亲疏水性转变和构象变化，智能高分子开关膜也能根据外部刺激改变自身的表面/界面特性、渗透通量或选择透过性。智能高分子膜被用作抗污染滤膜、亲和分离、酶反应的起/停控制以及控制释放等。智能高分子开关膜的制备方法直接影响其环境刺激响应特性、稳定性和可重复制备性等。因此，系统介绍了基材膜修饰法、基材修饰成膜法和共混成膜法等3种智能高分子开关膜制备方法的定义、分类、机理和研究进展，并对比了3种方法的优缺点。基材膜修饰法研究最多，而共混成膜法最有望用于大规模制备智能高分子膜。本文以期为高效制备具有稳定、优良响应特性的智能高分子开关膜提供指导和参考。

[关键词]　智能高分子膜；智能凝胶；智能线性高分子；制备方法；相转化法
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1　前言

人类科技的进步与发展离不开大自然的启发，比如受鸟类启发发明飞机，受蝇眼启发发明蝇眼照相，受荷叶的微纳结构启发构筑了人工自清洁表面等。早在19世纪80年代，学者们受到生物膜选择透过性的启发，开始致力于环境刺激响应型智能高分子膜的研究[1, 2]。环境刺激响应型智能高分子膜是能够感知外界微小的化学、物理刺激，并作出响应改变自身的表面/界面特性、渗透通量或选择透过性的高分子膜材料[3~5]。与传统高分子膜相比，受生物膜启发的环境刺激响应型智能高分子膜具有环境响应的选择性和“开/关”特性[2]。因此，环境刺激响应型智能膜在化学物质/药物的控制释放、物质分离、水处理、组织工程、化学传感器等领域有着潜在的应用价值。目前，已有智能高分子膜被用作抗污染滤膜[6]、亲和分离[7]、酶反应的起/停控制[8]以及控制释放[9]等的报道。

按照智能高分子膜的结构，智能高分子膜可以分为智能高分子凝胶膜和智能高分子开关膜两种[4, 10]。智能高分子凝胶膜是由智能高分子交联而成的均质凝胶膜（见图1a），它在外界环境刺激的作用下会整体溶胀或收缩（见图1c），从而改变其渗透特性和选择透过性。智能高分子开关膜则是将智能高分子与非刺激响应型基材膜结合而成，智能高分子作为智能开关调节膜孔大小（见图1d），从而实现渗透特性和选择透过性的变化。智能高分子凝胶膜完全由交联的智能高分子凝胶组成，强度低，多见于智能微囊膜。而智能高分子开关膜能够结合基材膜的机械强度等方面的优异性能和智能高分子的环境刺激响应性能，研究最为广泛。值得注意的是智能高分子开关膜中的智能高分子开关可

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以是交联凝胶/微凝胶(图1a)也可以是线性高分子(图1b)。此外,智能高分子膜的形式可以是微囊膜、中空纤维膜和平板膜。

智能膜的类型多种多样。目前,已有关于温度响应型智能膜[11]、pH响应型智能膜[1]、离子强度响应型智能膜[12]、光响应型智能膜[13]、电场响应型智能膜[14]、磁场响应型智能膜[15]、特定化学物质[16]或离子响应型智能膜[17]、多重刺激响应型智能膜[18]的报道。其中,在众多的智能膜中温度响应型和pH响应型智能膜的研究最为广泛。目前报道的温度响应型智能膜主要是基于聚(*N*-异丙基丙烯酰胺)(poly(*N*-isopropylacrylamide),PNIPAM)的酰胺类高分子,它的低临界溶液温度(lower critical solution temperature,LCST)与人体温度接近,且响应速度快。而pH响应型智能膜主要是基于聚丙烯酸(PAA)的聚弱电解质。

智能高分子开关膜的环境刺激响应特性、稳定性、可重复制备性等重要参数一定程度上取决于膜的制备方法,因此本文将着重介绍智能高分子开关膜的各种制备方法及其优缺点,以期为制备甚至大规模生产具有稳定、优良响应特性的智能高分子开关膜提供指导和参考。

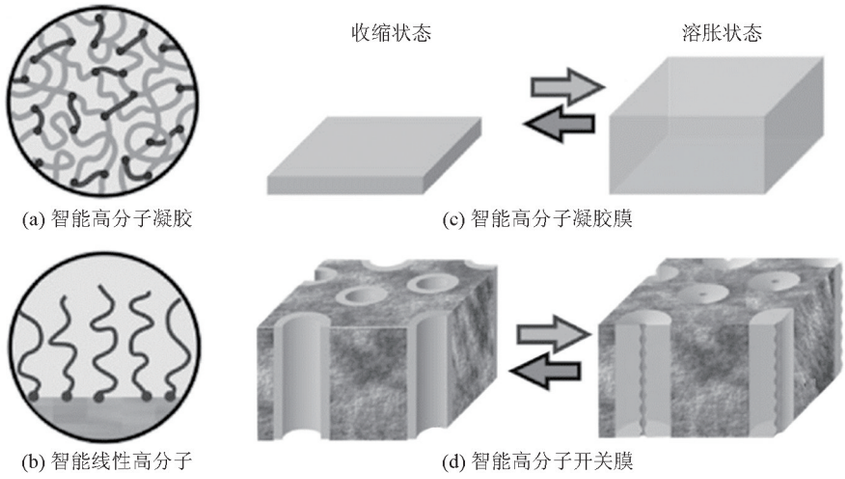

图1　环境刺激响应型智能高分子膜的分类 (修改自参考文献[10])

Fig. 1　Classification of stimuli-responsive smart polymeric membranes (modified from Ref. [10])

2　智能高分子开关膜的主要制备方法

用于制备智能高分子开关膜的基膜材料可以是亲水性材料,比如聚酰胺类(尼龙6,N6)和纤维素类(醋酸纤维素)等,但主要还是疏水性材料,比如聚砜类、聚醚砜(PES)、烃类聚合物(聚乙烯、聚丙烯)、氟代烃类聚合物(聚偏氟乙烯(PVDF)、聚四氟乙烯)、聚酯类(聚对苯二甲酸乙二醇酯、聚碳酸酯)等。这些膜材料不具有环境刺激响应的特性,因此需要将智能高分子材料添加到基材膜中。智能高分子开关膜可以通过物理方法或者化学方法将智能高分子与基材膜结合得到。物理方法包括填充(filling)或共混(blending)等,该方法操作简单,但制备的智能高分子与膜材料结合稳定性低、分布均匀性差。化学方法包括化学接枝法、等离子体接枝法、光接枝法、射线接枝法等。采用化学方法制备智能高分子开关膜,智能高分子和基材膜通过稳定的共价键结合,因此得到的智能膜也具有稳定的环境刺激响应特性。但它通常会借助化学试剂或外源高能物种对基材膜进行改性,对设备和制备条件要求高。根据智能高分子引入基材膜的时间,智能高分子开关膜的制备方法可以分为基材膜修饰法(成膜后添加智能高分子)、基材修饰成膜法(成膜前添加智能高分子)和共混成膜法(成膜中添加智能高分子),如图2所示。

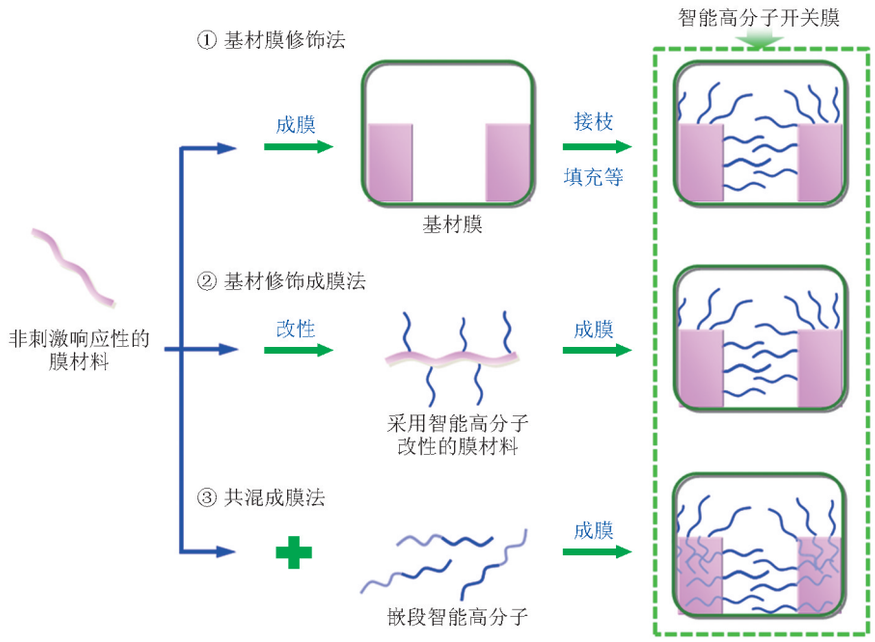

图2　智能高分子开关膜的制备方法分类

Fig. 2　Different preparation methods of smart polymeric gating membranes

2.1　基材膜修饰法

基材膜修饰法顾名思义即在多孔的基材膜上，在不改变基材膜主体结构的情况下，通过物理方法（比如填充（filling）等）或化学方法（各种接枝法（grafting））在膜表面和孔内引入智能高分子开关，如图2a所示。基材膜修饰法可选择的基材膜材料范围很大，且易于分析基材膜及引入智能高分子开关后的智能膜的孔结构与孔径大小，从而有助于研究智能高分子开关膜的响应机理和环境刺激响应性能与结构的关系。因此，这种方法是最早采用也是迄今为止研究最多的智能膜制备方法[1]。

Li等[9]将多孔N6基材膜浸没在*N*-异丙基丙烯酰胺（NIPAM）单体溶液中，并引发自由基聚合得到膜孔中物理填充PNIPAM智能凝胶的温度响应型智能膜。与物理方法相比，采用化学接枝方法制备智能高分子开关膜研究更为广泛。按照不同的聚合机理，化学接枝法可分为“接枝自”（grafting from）和“接枝到”（grafting to）两种方法。“接枝自”方法是在惰性的基材膜表面产生活性位点，然后从这些活性位点出发引发功能单体聚合，从而产生与基材膜共价连接的智能高分子开关。“接枝到”方法则是将预先聚合的智能高分子共价地结合到基材膜上，预先聚合的智能高分子和基材膜需要带上可以相互反应的活性基团。通常，智能高分子和基材膜的相互反应是基于巯基/双硫键与金的键合、氨基与醛的加成反应、氨基与环氧键的亲核取代反应等。由于篇幅原因，这里仅介绍常见的“接枝自”方法制备智能高分子膜的研究进展。基材膜表面活性位点可以通过外源高能物种（如γ射线[19]、紫外（UV）、等离子体、氧化还原对等）激发发生均裂而形成，也可以通过化学修饰带上自由基引发剂。

等离子体接枝法是在一定的气氛放电产生低温等离子体，与等离子体接触的基材膜表面会产生大量活性位点，之后导入单体溶液便能引发智能高分子开关接枝在膜表面上。根据气氛的不同，等离子体可以分为氨气等离子体接枝法、氩气等离子体接枝法、氢气等离子体接技法、空气等离子体接枝法等。它们都可以用于制备各种刺激响应类型的智能高分子开关膜[20~23]。

UV光接枝法需要借助Ⅱ型光引发剂在UV光照下从其他分子上夺氢的特点在膜表面产生活性位点，从而引发单体在膜表面接枝聚合[24]。目前常常采用二苯甲酮和安息香乙醚作为光引发剂在UV光照条件下制备pH响应型和温度响应型智能高分子开关膜[25, 26]。

氧化还原对（redox pair）可以作为引发剂引发单体在基材膜表面的接枝共聚，这种方法可以称为氧化还原接枝法。目前报道的氧化还原对有强氧

化剂硝酸铈铵与还原性基团(如醇羟基、醛、酮、胺和酰胺等)和亚硫酸钠–过硫酸钾等。该方法可以在尼龙膜、醋酸纤维素和聚醚砜类基材膜上接枝pH响应型和温度响应型智能高分子开关,从而得到相应的智能高分子开关膜[1, 27]。氧化还原接枝法反应条件温和,操作方便,但是会产生较多的均聚物。

原子转移自由基聚合(atom transfer radical polymerization, ATRP)接枝法能够利用特定类型的卤代烃作为自由基聚合的引发剂,比传统自由基引发剂更容易通过化学反应共价结合到膜上,从而在一定的催化条件下引发功能单体的聚合。常见的卤代烃引发剂为2-溴异丁酰溴(2-bromoisobutyryl bromide, BIBB)。ATRP是一种可控自由基聚合方法,相较于传统自由基聚合,该方法能很好地抑制自由基转移反应,从而很好地控制智能高分子链的长度和接枝率等。采用ATRP方法不仅能够制备具有均聚或无规共聚的智能高分子开关的智能膜[7,28],还能得到具有嵌段智能高分子开关的智能膜[29]。由于嵌段聚合物中的每一嵌段能够很好地保持各自的物化特性,与无规共聚相比能提供更广阔的分子结构设计空间,从而制备出结构、性能更为优越的智能高分子开关膜。

2.2 基材修饰成膜法

基材修饰成膜法是在成膜之前对高分子膜材料进行化学改性从而引入智能高分子,然后将化学改性的膜材料制备成智能膜,如图2b所示。通常用于基材修饰成膜法的高分子膜材料是疏水性的,制备智能高分子膜的方法是相转化法。智能高分子材料可以通过无规共聚或嵌段共聚引入基材膜材料中。无规共聚主要应用于可以从单体的加聚反应获得高分子的膜材料,如(氟代)烃类聚合物和聚丙烯腈。Kobayashi等[30]通过丙烯酸、甲基丙烯酸与丙烯腈的无规共聚获得共聚高分子,然后利用相转化法制备了pH响应型聚丙烯腈超滤膜。而嵌段共聚则是通过如γ射线接枝法[31, 32]、化学接枝法[33]、ATRP接枝法[34]以及臭氧预处理[35~38]等方法对高分子膜材料直接进行化学修饰,从而引入智能高分子。Kang等[34]采用ATRP接枝法从PVDF主链上引发甲基丙烯酸*N*,*N*-二甲氨基乙酯(DMAEMA)的聚合,通过控制反应的时间,可以控制接枝链的长度,从而改变制备的pH、温度双重刺激响应型膜的形貌和分离特性。针对较难改性的氟代聚烯烃高分子PVDF,新加坡国立大学的Kang等[35~38]开发了采用O_3对PVDF高分子进行预处理的技术。该技术可以使PVDF主链上带上过氧基团,进而热引发自由基聚合、可逆加成–断裂链转移可控自由基聚合(RAFT)亲水性功能单体,制备以PVDF为主链的两亲智能高分子或者具有功能接枝侧链的两亲高分子。随后,再将得到的两亲智能高分子采用相转化法制备出温度响应型、pH响应型、pH和温度双重刺激响应型的智能高分子膜。图3是采用臭氧对PVDF进行预处理并热引发自由基接枝聚合得到PNIPAM-*g*-PVDF高分子、然后利用相转化法制备温度响应型智能PVDF膜的示意图。在相转化法制备智能高分子膜过程中,含有两亲高分子的铸膜液在含水的凝固浴中固化时,亲水的高分子链会在膜孔形成的过程中大量富集到膜孔表面,从而自发地形成膜孔表面“接枝”有环境刺激响应高分子开关的智能高分子膜[39]。

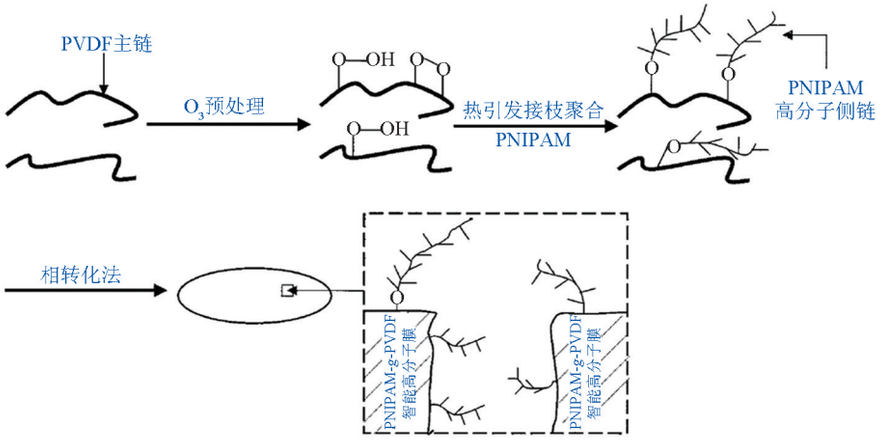

图3 臭氧预处理PVDF高分子并热引发NIPAM聚合及制备温度响应型智能膜过程示意图[35]

Fig. 3 Schematic illustration of thermo-induced polymerization on ozone-pretreated PVDF polymer and fabrication of thermo-responsive membrane [35]

2.3 共混成膜法

共混成膜法是在成膜过程中先物理共混智能高分子材料，紧接着采用相转化法制备智能高分子开关膜，如图2c所示。添加的智能高分子材料可以是交联凝胶，也可以是线性高分子；可以是亲水的均聚物，也可以是无规共聚或两亲嵌段共聚高分子。这里的两亲嵌段高分子的疏水嵌段不同于基材膜材料，但它是容易合成、物化性能优异且与基材膜材料相容性好的高分子材料，以保证两亲嵌段高分子在智能膜材料中的稳定性。

Wang等[40]在海藻酸钙毫米囊的凝胶囊壁中物理共混了PNIPAM纳米凝胶，制备得到了温度响应型智能毫米囊。类似地，Wang等[41]和Song等[42]在PES铸膜液中物理共混PNIPAM纳米凝胶，再通过相转化制备了具有温度响应性和乙醇浓度响应性的智能高分子开关膜。Kang等[43]将PNIPAM与PAA-*g*-PVDF高分子膜材料共混，再用相转化法制备了智能高分子PVDF膜。由于PNIPAM可以与PAA-*g*-PVDF膜材料的PAA高分子链之间产生氢键作用，PNIPAM高分子可以稳定地留在多孔的PVDF膜中，所制备的膜具有pH及温度双重响应特性。

Jiang等[6]采用分步加料的自由基聚合法合成了化学组成类似于嵌段聚合物的聚甲基丙烯酸正丁酯–嵌段–聚甲基丙烯酸–嵌段–聚甲基丙烯酸六氟正丁酯（PBMA-*b*-PMAA-*b*-PHFBM）。该三嵌段聚合物与PES共混，利用相转化法制备了具有pH响应特性的智能高分子PES膜。采用分步加料的自由基聚合法，当改变单体的投料量时，可以改变嵌段聚合物各个嵌段的含量。Zhu等[44]在一种商品化的两亲三嵌段高分子F127（poly(ethylene oxide)$_{100}$-*block*-poly(propylene oxide)$_{65}$-*block*-poly(ethylene oxide)$_{100}$）两端共价连接ATRP引发剂2-溴异丁酸酯，然后通过ATRP反应在三嵌段的F127的两端共聚上不同聚合度的聚丙烯酸*N*,*N*-二甲氨基乙酯（PDMAEMA）嵌段，获得F127-*b*-PDMAEMA五嵌段聚合物；然后将F127-*b*-PDMAEMA五嵌段聚合物与PES共混，利用相转化法制备pH、温度双重响应的智能高分子PES膜。该研究中F127-*b*-PDMAEMA高分子结构可控，可以方便地通过改变PDMAEMA嵌段的聚合度在一定程度上调整膜的刺激响应性通量变化；但是该智能高分子膜的缺点在于F127-*b*-PDMAEMA的五嵌段聚合物水溶性不利于其长期稳定地留在PES膜中。Luo等[45]采用ATRP方法成功制备了具有相同疏水嵌段链长度，不同亲水嵌段链长度的两亲嵌段聚苯乙烯–嵌段–聚丙烯酸（PS-*b*-PAA）高分子，并与PES膜材料共混后通过相转化法成膜（见图4）。该研究实现了添加两亲嵌段高分子的精确控制，从而获得pH响应性能可控的智能膜。

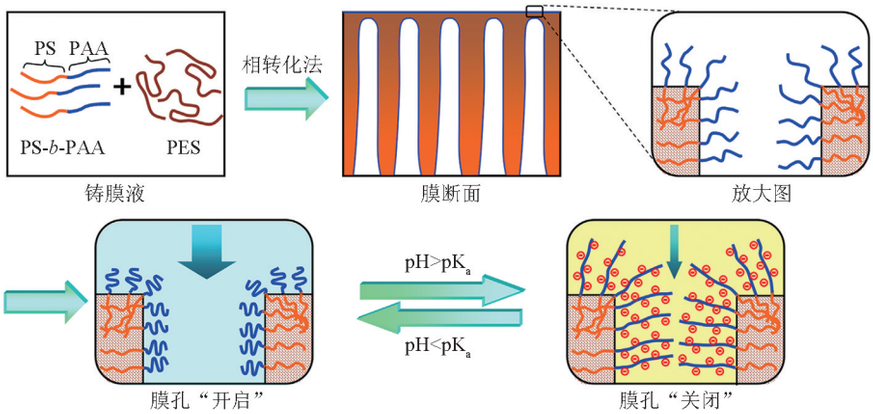

图4 共混两亲嵌段PS-*b*-PAA高分子制备pH响应型智能PES膜的示意图（a~c）及其pH响应开关特性（d，e）[45]

Fig. 4 Schematic illustration of fabrication process (a~c) and pH-responsive gating function (d, e) of pH-responsive PES membranes blended with amphiphilic PS-*b*-PAA block polymers[45]

3 结语

制备智能高分子开关膜的方法可以分为基材膜修饰法(成膜后添加智能高分子)、基材修饰成膜法(成膜前添加智能高分子)和共混成膜法(成膜中添加智能高分子)。

基材膜改性法适用的基材膜种类多、方法多种多样,易于表征智能高分子开关的含量和智能膜的结构,研究较广泛;但是,往往改性后智能膜的孔径较基材膜有所减小,渗透通量也会相应减小。目前的改性方法针对微孔尺寸的膜孔改性比较有效,膜孔越小,整个膜断面上孔内的改性越难。改性方法的可重复性欠佳,个别方法如γ射线接枝法和等离子体接枝法对设备要求高,目前尚不适用于大规模制膜。

采用基材修饰成膜法制备智能高分子开关膜,智能两亲高分子的疏水嵌段构成膜主体,而亲水嵌段则作为智能膜孔中共价接枝的智能高分子开关。因此,基材修饰成膜法能够实现对智能高分子开关膜整个断面的孔进行化学改性。但是,基材修饰成膜法通常是PVDF、聚砜类、PES等疏水性膜材料,化学改性的难度较大。与γ射线接枝法相比,臭氧预处理方法适合用于大规模生产,但该方法迄今尚难以对智能两亲高分子的结构进行控制。

共混成膜法成膜的过程简单,有望实现智能高分子开关膜的大规模制备。该法制备智能高分子开关膜的难易度取决于智能高分子的制备。当添加均聚或无规共聚高分子作为智能高分子时,方法简单易行,有望用于大规模生产智能高分子开关膜。当采用两亲嵌段聚合物作为智能高分子时,可以借助ATRP等可控自由基聚合方法对智能高分子的结构精确控制,从而精确调控智能高分子开关膜的环境刺激响应特性。

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Advances in preparation methods of smart polymeric gating membranes

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[**Abstract**] Smart polymeric gating membranes are composed of smart polymers and non-stimuli-responsive substrate membrane. The smart membranes can automatically change the hydrophilicity/hydrophobicity on the surface as well as trans-membrane permeability and selectivity in response to the environmental stimuli, which is attributable to the stimuli-responsive variation of hydrophilicity/hydrophobicity and configuration of the smart polymers in the membrane. Smart polymeric gating membranes are used for anti-fouling filtration, affinity separation, "on/off" control of enzyme reaction and controlled release, etc. The way to prepare such membranes affects the important parameters of smart polymeric gating membranes, such as the stimuli-responsive characteristics, stability and reproducibility. There are three kinds of preparation methods to fabricate the smart polymeric gating membranes according to when the smart polymers are added into the membrane materials. They are the methods introducing smart polymers by the modification of substrate membranes materials after membrane preparation, by the modification of substrate membrane materials before membrane preparation and by blending smart polymers during the membrane preparation. The definitions, subcategory, mechanisms and new advances of these preparation methods are introduced separately, and their advantages and disadvantages are addressed. The method that introduces smart polymers by the modification of substrate membranes materials after membrane preparation is the most widely employed to form the smart polymeric gating membranes. However, the method that blends smart polymers during the membrane preparation has great potentials to the mass production of smart polymeric gating membranes in the future. This paper will provide valuable guidance for the efficient preparation of smart polymeric gating membranes with stable and satisfactory stimuli-responsive characteristics.

[**Key words**] smart polymeric membranes; smart cross-linked gel; smart linear polymer; preparative method; phase inversion