高 分 子 学 报
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·综述·

开环易位聚合诱导自组装

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摘 要 聚合诱导自组装(PISA)已成为一种高效合成固含量高、形貌多样纳米颗粒的新方法，在高分子化学和纳米材料等领域引起了广泛关注. 近年来，面向环烯烃单体的开环易位聚合(ROMP)具有可控性好、官能团耐受性高、适配大位阻单体等优势，越来越多地应用于聚合诱导自组装领域，成功获得系列主链含有不饱和双键的聚合物纳米颗粒. 本综述聚焦开环易位聚合诱导自组装(ROMPISA)，从有机相、水相和有机/水相三个方面，总结开环易位聚合诱导自组装在纳米颗粒形貌控制、功能调控以及应用等方面的研究进展，同时探讨了相关领域存在的机遇与挑战，希望为聚合诱导自组装领域的发展提供借鉴.

关键词 开环易位聚合；聚合诱导自组装；嵌段共聚物；纳米颗粒

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聚合诱导自组装(PISA)是近年来发展起来的高效制备纳米颗粒(nano-objects)的新方法[1,2]. 基本原理是，以亲溶剂的第一嵌段为大分子引发剂(macro-initiator)或大分子链转移剂(macro-CTA)，加入第二单体(成核单体)进行扩链聚合反应获得嵌段共聚物. 由于生成的第二嵌段无法溶解于溶剂，链增长过程伴随着两亲性嵌段共聚物的相分离形成纳米颗粒，聚合反应与自组装过程同步进行，反应体系由均相转变为非均相直至单体消耗完毕(图1(a))[3,4]. 与传统方法相比，聚合诱导自组装制备纳米颗粒具有速度快[5,6]、固含量高[7~9]、形貌多样[10,11]等特点，通过引入刺激响应基团[12~14]、动态共价键[15]、降解位点[16~18]等，高效制备出一系列不同结构和功能的纳米颗粒，已成为高分子化学和纳米材料等领域的研究热点.

不同机理的可控聚合方法，均可以应用于聚合诱导自组装，包括原子转移自由基聚合(ATRP)[19~23]、可逆加成−断裂链转移自由基聚合(RAFT)[24~28]、氮氧自由基聚合(NMP)[29~33]、阴离子聚合(LAP)[34~36]、开环聚合(ROP)[37~42]、开环易位聚合(ROMP)[43]等. 其中，以RAFT为代表的可控自由基聚合在聚合诱导自组装方面的研究最为广泛和深入[44~47]，不仅制备出球形(s)、蠕虫(w)、囊泡(v)等基本形貌[48~51]，并且获得了水母(jellyfish)、补丁(patchy)等特殊高级形貌[52~55]，在生物医学等诸多领域获得了应用[56~60].

开环易位聚合是将环烯烃单体转化为主链含有不饱和双键聚烯烃的良好方法，具有可控性好、官能团耐受性高、适配大位阻单体等优势[61,62]. 开环易位聚合遵循链式聚合机理，包含链引发、链增长和链终止三类基元反应(图1(b))[62,63]. 在均相聚合研究基础上，非均相开环易位聚合同样受到了关注，包括分散ROMP[64,65]、乳

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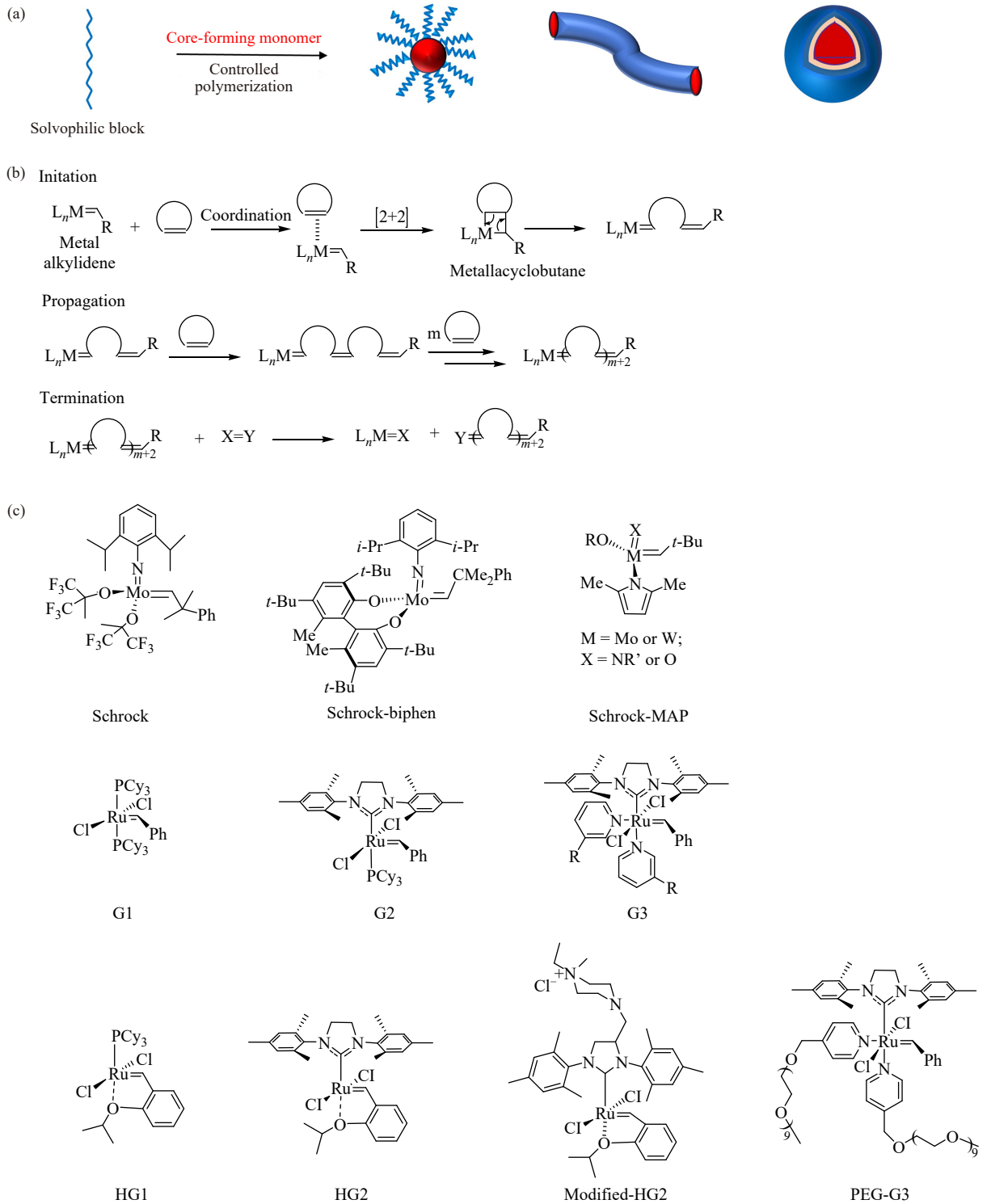

Fig. 1 (a) Ring-opening metathesis polymerization induced self-assembly (ROMPISA); (b) Ring-opening metathesis polymerization (ROMP) mechanism; (c) Catalysts for ROMP.

液ROMP[66,67]、悬浮ROMP等[68]. 开环易位聚合诱导自组装(ROMPISA)继承了ROMP的特点，属于特殊的非均相聚合，无需添加额外的乳化剂或稳定剂，高效获得固含量高、形貌多样、含有不饱和双键的聚合物纳米颗粒，可进一步用于点击化学[69,70]、交联反应[71,72]、化学修饰[73]等. 自2010年首次报道以来，得益于催化剂的迭代和部分商品化(图1(c))，开环易位聚合诱导自组装(ROMPISA)由最初的有机相体系扩展到水相和有机相/水相体系，成为聚合诱导自组装领域研

究的重要板块.

本综述聚焦开环易位聚合诱导自组装制备纳米颗粒，从有机相、水相、有机/水相三种反应介质角度，总结了纳米颗粒形貌控制、功能调控以及应用等方面的研究进展，并且对相关领域存在的机遇与挑战进行了展望.

1 有机相开环易位聚合诱导自组装

作为开环易位聚合的关键因素，催化剂目前主要包括 Schrock 和 Grubbs 2 类[74~76]. Schrock 催化剂以高氧化态钼(Mo(VI))或钨(W(VI))为金属中心、强供电子烷氧基和亚胺基为配体，活性高，立体控制性好，但是对空气和水等极度敏感[76~78]. Grubbs 催化剂以低氧化态钌(Ru(II))为金属中心，从双膦配体(G1)到*N*-杂环卡宾配体取代 1 个膦配体(G2)[79]、*N*-杂环卡宾配体和吡啶配体取代 2 个膦配体(G3)[80]. Grubbs 催化剂的立体控制性不如 Schock 催化剂好，但是无需严格的无水无氧操作，官能团耐受性高，适配大位阻单体，在有机溶剂中表现出优异的溶解性[81,82]，并且可以商品化获得，因此基于 Grubbs 催化剂的有机相开环易位聚合诱导自组装成为了理想的研究对象.

1.1 无额外驱动力

2010 年，Xie 等[83]首次基于 Grubbs 一代催化剂(G1)实现了有机相(甲苯)中的开环易位聚合诱导自组装(图 2). 首先在甲苯中催化 2,3-双(2-溴异丁酰氧甲基)-5-降冰片烯(BNBE) ROMP 制备亲溶剂嵌段，随后加入 7-氧杂降冰片-5-烯-外型，外型-2,3-二甲酸二甲酯(ONBDM)单体进行扩链. 随着反应进行，原位生成的两亲性嵌段共聚物 PBNBE-*b*-PONBDM 发生自组装，形成 PONBDM 嵌段为核、溴官能化 PBNBE 嵌段为壳的球形纳米颗粒，粒径分布在 140~200 nm 之间. 壳层中引入的溴原子既可以作为 ATRP 的引发剂，也可以与甲基咪唑反应生成离子液体用于催化二氧化碳固定等反应. 在扩链时加入外型-*N*-(肉桂酰氧乙基)-7-氧杂降冰片-5-烯-2,3-二甲酰胺(CONBI)，紫外光照下 CONBI 中的双键发生反应，制备了核交联的纳米颗粒，稳定性获得了提升[84].

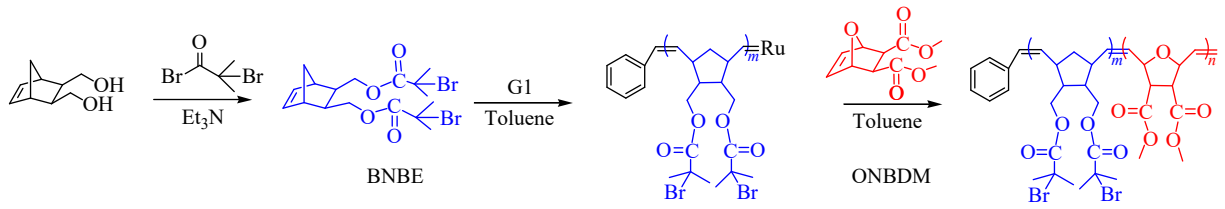

Fig. 2 Synthesis of PBNBE-*b*-PONBD diblock copolymer vesicles *via* ROMPISA.

2016 年，Cho 等[85]利用 ROMPISA 合成了多硫烷功能化聚降冰片烯的纳米颗粒. 利用 G3 催化剂在有机溶剂中引发*N*-环己基-外-降冰片烯-5,6-二甲酰亚胺(ChNDI)形成亲溶剂嵌段，加入环状多硫烷单体(CPM)进行扩链. 研究表明，增加 CPM 嵌段的聚合度，可使纳米颗粒尺寸增大，同时提高了纳米颗粒的折射率，折射率在 1.54~1.65 范围之间.

2017 年，Gianneschi 等[86]利用 ROMP 可聚合大位阻单体的特性，以含肽链降冰片烯衍生物为扩链单体，在混合有机溶剂中，通过 G3 催化实现了 ROMPISA，生成了含肽链的嵌段共聚物纳米颗粒(图 3). 通过对 DMF/MeOH 混合溶剂体系的系统筛选，确定了 *V*:*V*=1:2 配比为最佳条件，制备出了均一的球形纳米颗粒. 亲溶剂嵌段的长度是调控纳米颗粒形貌的决定性因素，随着亲溶剂嵌段的缩短，亲溶剂性及空间排斥效应显著减弱，导致曲率降低，驱动形貌由高曲率的球形逐渐向低曲率的蠕虫状及囊泡演变. 该 ROMPISA 体系在 20 wt%的固含量条件下保持了典型的活性聚合特征，获得了高单体转化率(>99%)和低分散度(*Đ*<1.2)，这种含肽链功能化纳米颗粒有望为疾病治疗提供新途径.

2019 年，Delaittre 等[87]将氮氧自由基(TEMPO)引入到亲溶剂嵌段，以 G1 为催化剂、降冰片烯为第二单体，在乙醇/四氢呋喃溶剂中通过 ROMPISA 制备了氮氧自由基功能化的纳米颗粒(图 4(a)). 该 ROMPISA 具有较快的反应动力学，仅需在室温下反应数分钟，即可高效制备出粒径在 10~110 nm 范围内的纳米颗粒，表现出良好的生物相容性(图 4(b))，并且在体外氧化应激模型中可以有效清除 ROS. 另一方面，在 Anelli 氧化

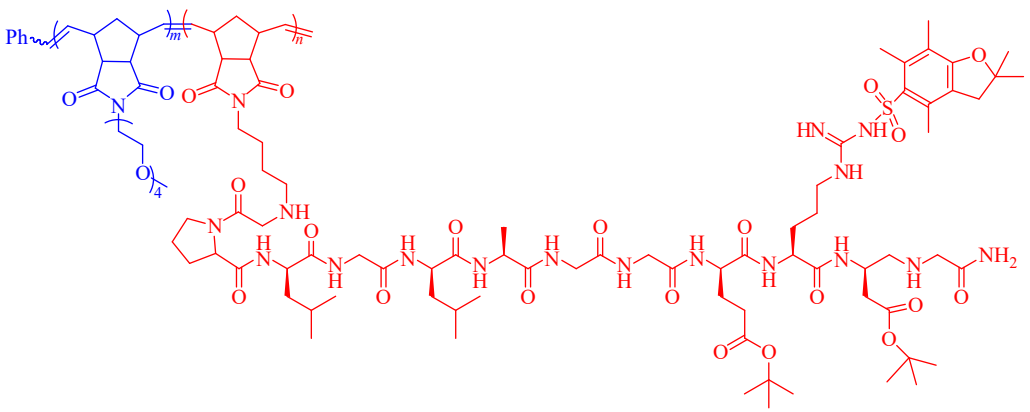

Fig. 3 Structure of the polymer peptide amphiphiles synthesized *via* ROMPISA.

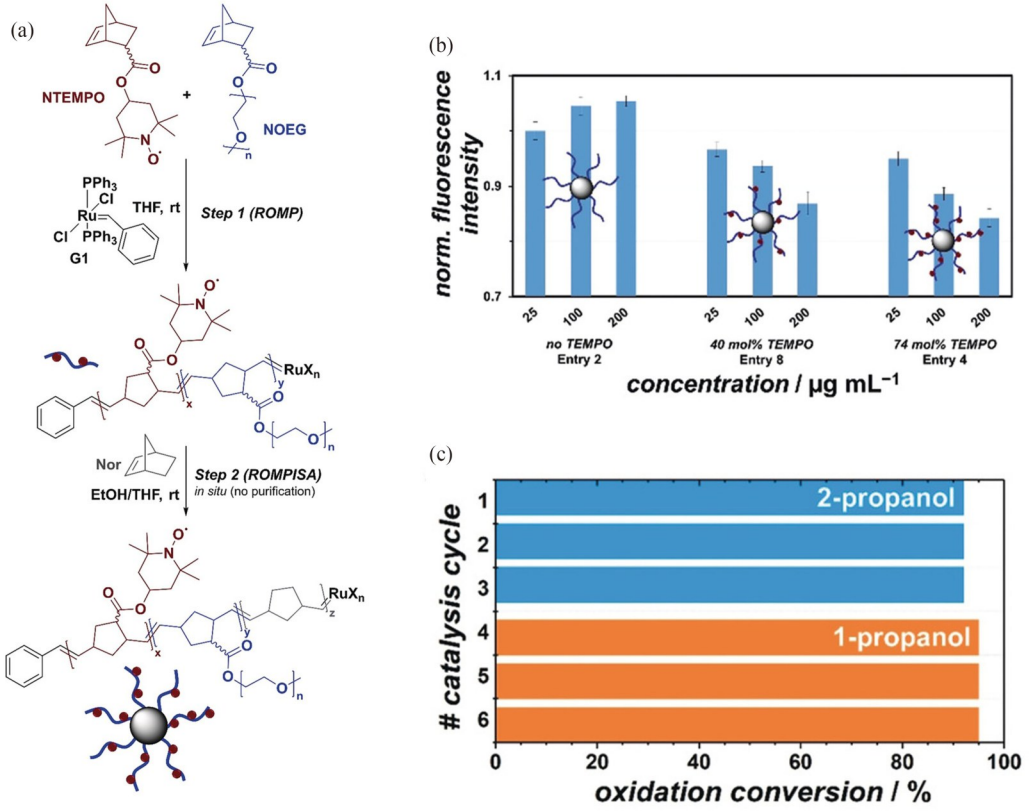

Fig. 4 (a) Tandem ROMPISA strategy for preparing nitroxide-functionalized polymer nanoparticles; (b) Results of the cytotoxicity study with WST-1 assays; (c) Recycling of radical nanoparticles for catalytic oxidation (Reprinted with permission from Ref. [87]; Copyright (2019) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

条件下，纳米颗粒将脂肪醇、芳香醇及低聚乙二醇等多种底物定量转化为相应的醛、酮和羧酸(转化率>98%)，还可以高选择性地将甲基*α*-*D*-吡喃葡萄糖苷的伯醇氧化为羧酸，其他官能团不受影响. 反应结束后，TEMPO功能化纳米颗粒通过离心高效回收，6次循环后仍保持活性和结构完整性，展现出均相催化、异相回收的优势(图4(c)).

2021年，Zheng等[88]以含双键聚己内酯(PCL)作为第一嵌段、双环戊二烯(DCPD)为成核单体，在多种有机溶剂中进行ROMPISA获得了交联纳米颗粒(图5). 含有双反应位点的DCPD在PCL中的双键位置“插入”，形成以交联聚双环戊二烯(PDCPD)为核的纳米颗粒. 通过改变甲苯、氯仿、四氢呋喃(THF)、1,4-二氧六环、*N*,*N*-二甲基乙酰胺等溶剂种类，调节溶剂与PCL的相互作用参数(χ_{12})，PCL嵌段的长度或PCL与PDCPD的质量比可以有效调控界面曲率，获得

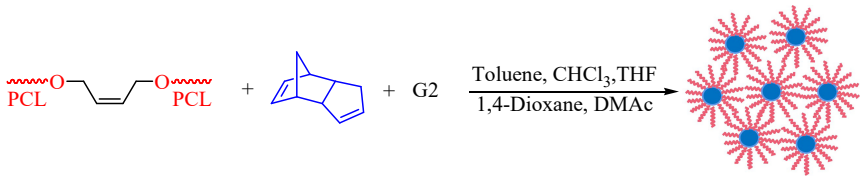

Fig. 5 Preparation of crosslinked PDCPD nanoobjects *via* ROMPISA.

球形、蠕虫等不同形貌的交联聚合物纳米颗粒. Zheng 等[89]在三羟甲基丙烷三缩水甘油醚(TMPTGE)与4,4′-亚甲基双(2-氯苯胺) (MOCA)组成的环氧前体中通过ROMPISA制备了纳米颗粒，固化后所得热固性材料的断裂韧性较纯环氧树脂显著提升. PCL嵌段的增长降低了颗粒的表面能与粒径，增大的界面面积强化了脱黏耗能，临界应力强度因子(KIC)和临界应变能释放率(GIC)随着PCL嵌段的增长稳步提升，增韧效果加强. 该工作揭示了纳米颗粒与宏观力学性能之间的关联，为热固性树脂的结构设计与性能提升提供了思路.

2024年，Shi等[90]报道了ROMP动力学控制的蠕虫纳米颗粒制备方法(图6)，通过改变溶剂性质、温度和π-π堆积效应等动力学因素，调控直径/长度和结构稳定性. 通过减少良溶剂二氯甲烷DCM的用量，或引入具有高T_g的成核嵌段，均可导致聚合物链运动能力下降，促进蠕虫状胶束的形成. 当升高温度时，室温下热力学亚稳态的蠕虫发生可控形貌演化，转变为囊泡结构. 当成核单体中含有芳环结构时，π-π堆叠增强了分子间作用力，或通过原位交联，均可增强蠕虫的结构稳定性. 在动力学捕获作用下，蠕虫形貌可在较宽DP范围内保持稳定，直径/长度均随DP的增加而逐步增大. 这种动力学控制的ROMPISA为PISA开辟了新路径，有望通过调控动力学因素制备“智能”高分子材料.

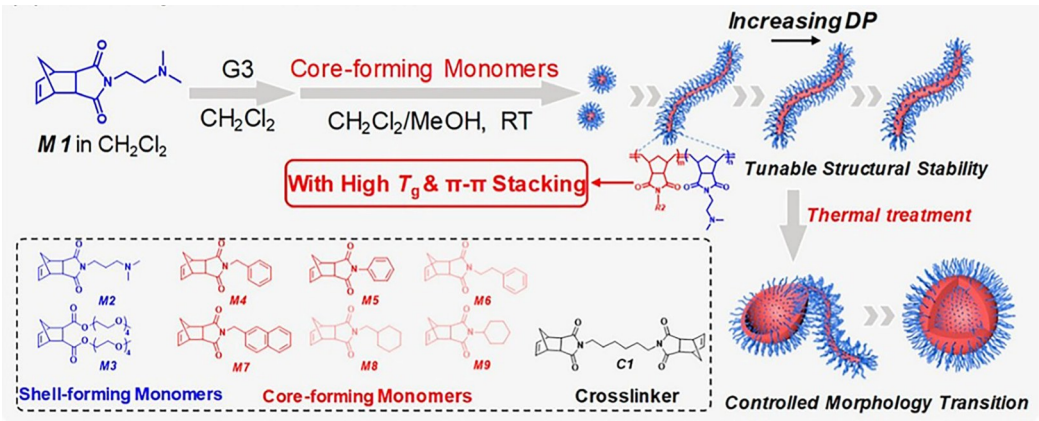

Fig. 6 Kinetically controlled ROMPISA for size-tunable and structurally stable worm-like micelles (Reprinted with permission from Ref. [90]; Copyright (2024) American Chemical Society).

1.2 π-π堆叠作用

π-π堆叠作为共轭结构的非共价相互作用，在导电高分子材料、晶体工程、有机光催化等多个领域具有重要应用[91]. 研究表明π-π堆叠可有效诱导聚合物的自组装行为，驱动纳米纤维、纳米管及复杂结构的形成，为设计新型功能材料提供了驱动力[92,93].

2012年，Choi等[93]以聚降冰片烯衍生物为第一嵌段(PN)、环辛四烯(COT)为扩链单体，在四氢呋喃(THF)、甲苯、二氯乙烷(DCM)中通过ROMPISA产生零维纳米颗粒，第二嵌段聚环辛四烯具有聚乙炔的结构(PA)，π-π堆叠作用为主要驱动力，实现从零维(0D)纳米颗粒原位形成(INCP)稳定的一维(1D)“纳米毛虫”(图7(a)). 嵌段共聚物(PN-*b*-PA) 零维纳米颗粒中，随着内核疏溶剂PA嵌段的增长，壳层亲溶剂PN嵌段的稳定作用逐渐减弱，内核之间有自发聚集和黏连的倾向，在PA嵌段中π-π堆叠作用的驱动下，零维(0D)纳米颗粒融合形成一维(1D)纳米毛虫，具有优异的热力学稳定性，在高温、超声辐射及强剪

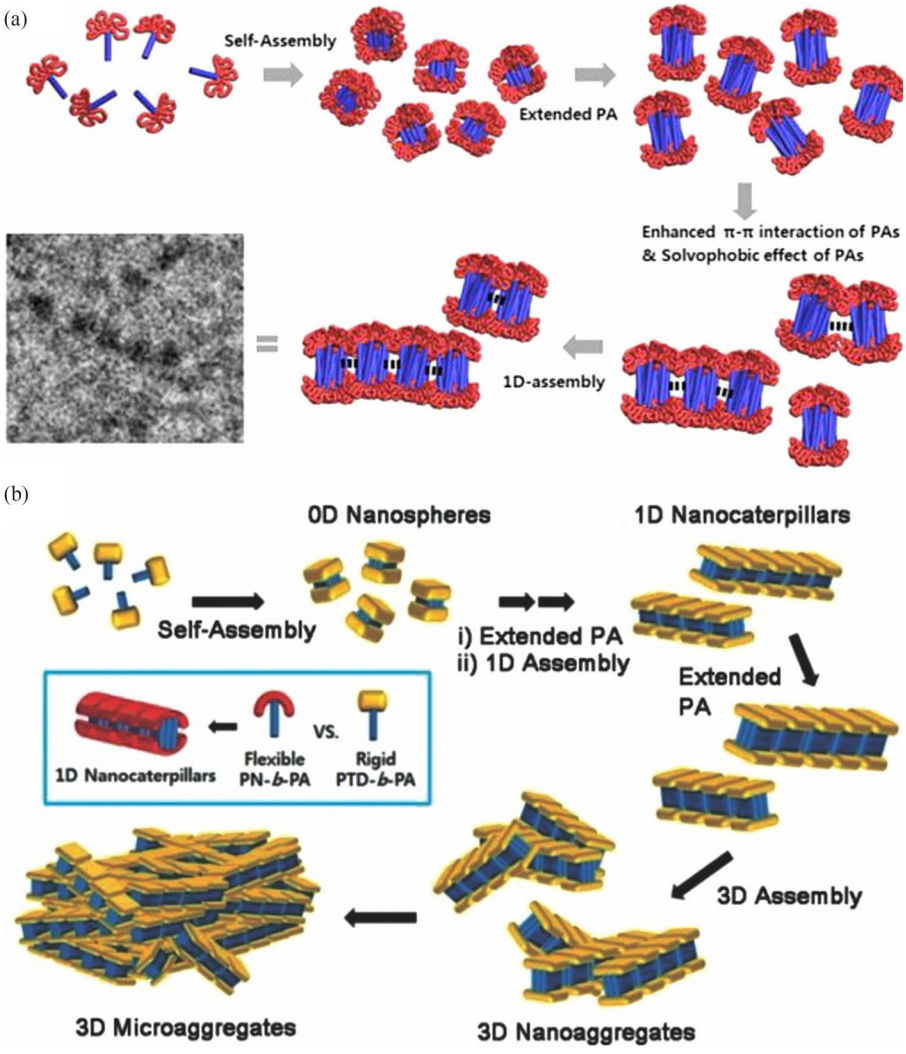

Fig.7 (a) Proposed mechanism for the *in situ* self-assembly of PN-*b*-PA into nanocaterpillars (Reprinted with permission from Ref. [93]; Copyright (2012) American Chemical Society). (b) Proposed schematic model of 3D microaggregate self-assembly *via* INCP (Reprinted with permission from Ref. [94]; Copyright (2015) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

切力等极端条件下仍能保持结构的完整性. 当内核疏溶剂PA嵌段的聚合度增加到一定程度时，一维结构的空间无法继续容纳不断增长的PA嵌段，纳米毛虫自发组装为三维纳米聚集体(3D-nano)和三维微米聚集体(3D-micro) (图7(b))[94].

前述工作也存在2大局限，一是聚环辛四烯(聚乙炔PA)为非等规立构，包含*E*和*Z*构型，二是一维纳米毛虫结构中存在纳米球缺陷. 针对上述问题，2014年，Choi等[95]优化了实验条件，通过改变ROMP的反应温度，控制了立体构型，制备出无缺陷的一维纳米毛虫结构. 在0 ℃低温条件下，ROMP抑制了链转移反应等副反应，有效消除了纳米球缺陷，获得由长链顺式PA核构成的均一“纳米毛虫”结构，还可以经热异构化转变为反式为主，纳米毛虫的尺寸和长度得以调控.

1.3 结晶驱动

结晶驱动自组装(CDSA)是大分子自组装的重要组成部分，以结晶、半结晶聚合物作为成核嵌段、结晶作为驱动力，通过“自成核”法或“种子生长”法，可以形成零维、一维、二维以及多维的复杂纳米颗粒，应用于纳米医学、催化剂载体、和光电子学等前沿领域[96,97].

2019年，Tang等[98]将结晶驱动引入ROMPISA，提出开环易位聚合诱导结晶驱动自组装(ROMPI-CDSA)新策略. 当选用复杂侧链的聚降冰片烯衍生物作为亲溶剂嵌段、以高结晶度(约38.3%)的聚二茂钌(PRc)作为成核嵌段时(图8(a))，通过结晶驱动自组装合成了透镜状的片晶. TEM的选区电子衍射(SAED)图案与原子力显微镜(AFM)进

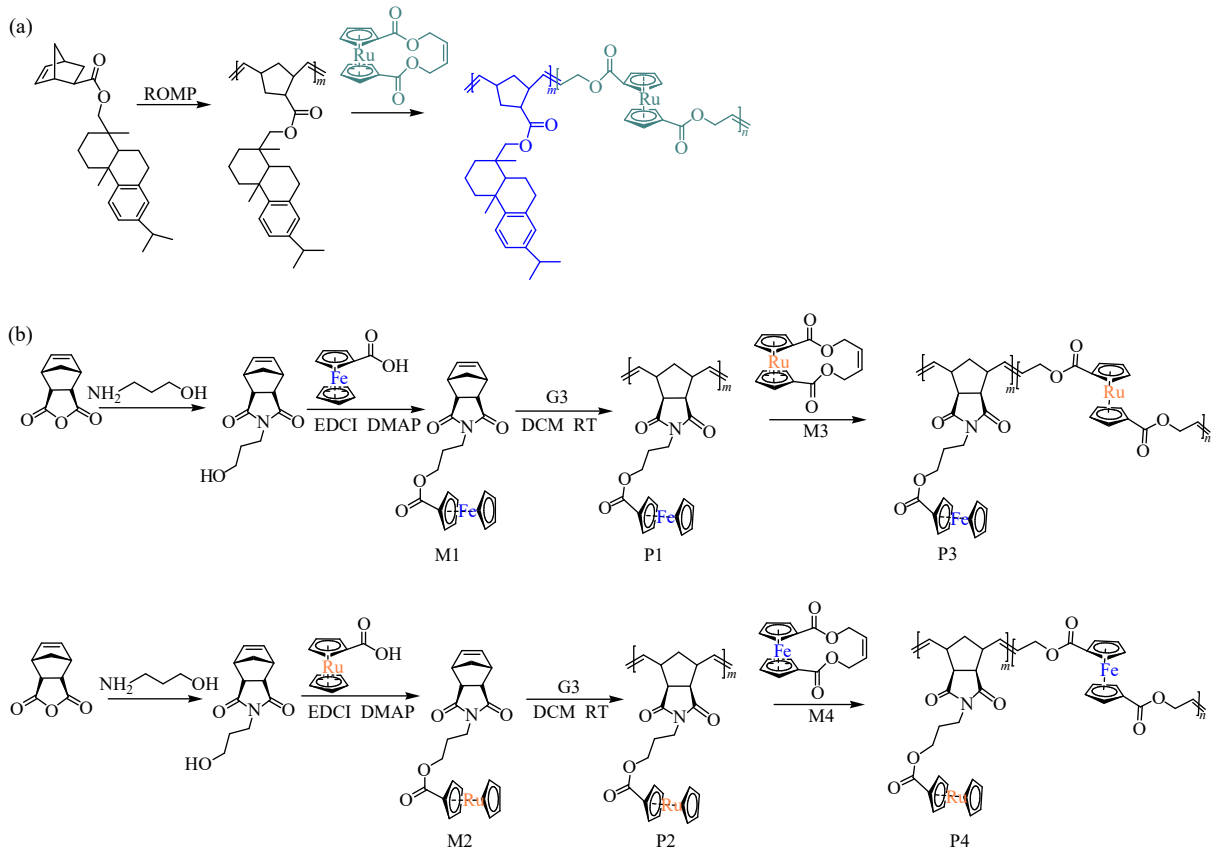

Fig. 8 (a) One-pot ROMPI-CDSA process enabling direct *in situ* assembly of block copolymers. (b) Synthesis of main-chain/side-chain type heterobimetallic block copolymers and illustration of their *in situ* self-assembly mechanism.

一步证明了结晶的PRc构成内核，具有明显的链折叠特征. 随着PRc嵌段聚合度的增加，形貌由纤维状逐步演化为以片晶为主的高阶结构.

2022年，Li等[99]通过ROMPI-CDSA成功合成了具有主链/侧链组合拓扑结构的异质双金属嵌段共聚物纳米颗粒(图8(b))，通过切换主链金属类型(Fe/Ru)，可调控该聚合物的光物理性质、电化学性能、热稳定性. 在$CHCl_3$中G3催化ROMP合成杂双金属嵌段共聚物P3和P4，P3 (Ru主链/Fe侧链)通过结晶驱动自组装(CDSA)形成具有Ru核-Fe壳结构的二维片晶；P4 (Fe主链/Ru侧链)则受疏溶剂作用驱动，形成Fe核-Ru壳结构. 这种主链金属类型的切换不仅实现了形貌的调控，更对聚合物的理化性质产生了影响，在光物理性质方面，通过切换主链金属，实现特定波段吸光能力的定向增强；在电化学性能方面，主链金属通过电子效应影响另一金属中心的氧化电位；在热稳定性方面，通过切换主链金属，可以调控初始分解温度和最终残炭量等热性能.

2 水相开环易位聚合诱导自组装

与有机溶剂相比，水作为绿色、环保的反应介质，在化学反应与化工过程中具有独特的优势. 然而，长期以来Grubbs催化剂(G1、G2、G3)限制于有机相催化，阻碍了水相ROMP以及ROMPISA的发展. 针对上述问题，通过在配体中引入季胺盐、聚乙二醇(PEG)等水溶性结构[100,101]，合成了适用于水相催化ROMP的改进型Hoveyda-Grubbs第二代催化剂(modified-HG2)、PEG配体修饰的第三代催化剂(PEG-G3)，具有较好的水相溶解性和聚合可控性，从而实现了开环易位聚合诱导自组装从有机相到水相的拓展.

2018年，Gianneschi等[102]利用水溶性阳离子季胺盐Hoveyda-Grubbs第二代催化剂(modified-HG2)，在纯水相中实现了ROMPISA. 首先通过水相ROMP制备刷形聚降冰片烯寡聚乙二醇(OEG)作为大分子引发剂，然后加入水溶性季铵盐功能化苯基降冰片烯二甲酰亚胺单体，通过ROMPISA形成了嵌段共聚物(图9(a))，固含量约

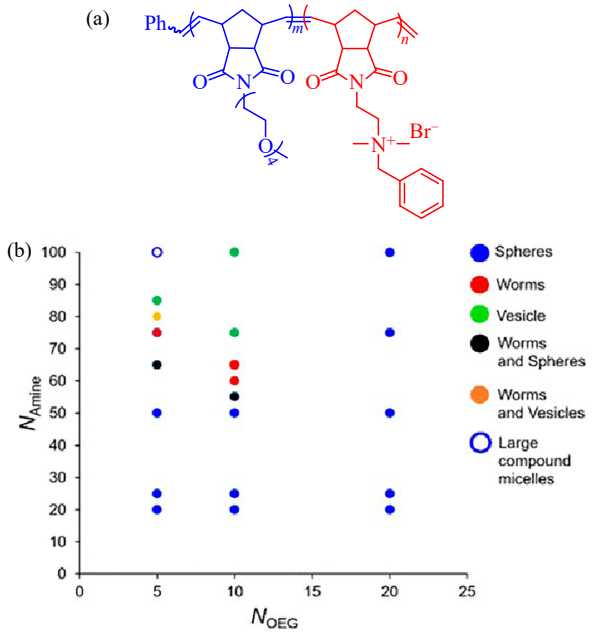

Fig. 9 (a) Molecular structure of an amphiphilic diblock copolymer used in ROMPISA; (b) Phase diagram of OEG-*b*-quaternary ammonium phenyl norbornene dicarboximide block copolymer particles prepared by ROMPISA in water at room temperature (Reprinted with permission from Ref. [102]; Copyright (2018) American Chemical Society).

20 wt%，聚合过程中分子量随单体转化率线性增长，且分散度始终维持在较低水平. 通过改变两个嵌段的长度，可以精确调控纳米颗粒的形状. 较长的亲水嵌段增大胶束外壳的体积，产生了更大的空间位阻，提高了胶束的曲率，促使嵌段共聚物自组装仅形成尺寸较小的球形胶束，反之较短的亲水嵌段，则可实现多形貌调控. 构建的不同亲/疏水嵌段长度的相图如(图9(b))所示，可以观察到蠕虫状胶束相区狭窄，随着囊泡内腔空间的填充会自发转变为大复合囊泡. 该研究有望用于制备面向生物医学应用的功能化纳米颗粒.

2019年，Giannesch等[103]在纯水相中制备了酶响应性纳米颗粒. 利用水溶性季铵盐修饰的Hoveyda-Grubbs第二代催化剂(modified-HG2)，以侧链含有识别序列(PLGLAG)的肽功能化降冰片烯作为亲水单体、季铵化苯基降冰片烯二甲酰亚胺衍生物作为成核单体进行扩链，通过ROMPISA合成了形貌均一的纳米颗粒. 聚合物链上的肽序列(GPLGLAGGWGERDGS)可以作为蛋白水解酶的底物，PLGLAG作为识别序列，在37 ℃下，酶能够精准识别并剪切肽侧基中的酰胺键，导致分子堆积参数改变，纳米颗粒转变为大聚集体. 利用这一酶响应特性，纳米颗粒在进入富含酶的病灶组织(例如肿瘤)后体积增大，无法扩散回血液循环，延长了药物在靶向部位的驻留时间. 与此同时，该团队将顺铂类似物通过共价键修饰在降冰片烯上作为成核单体，引入2-(二异丙氨基)乙基降冰片烯二酰亚胺(NB-DPA)作为pH响应单体，合成了pH响应性纳米颗粒，揭示了纳米颗粒的尺寸与表面电荷对细胞摄取及抗肿瘤药效的构效关系[104]. 在中性生理条件下纳米颗粒保持稳定(载药量达到20%)，而在模拟肿瘤微环境的弱酸性条件(pH=6.0)下，内核的二异丙氨基发生质子化，诱导由疏水向亲水的转变，触发纳米颗粒的快速解组装与药物释放. 细胞实验证实，小尺寸(约21 nm)表面带弱正电荷(+3.9 mV)的纳米颗粒表现出最佳的协同效应，细胞摄取量及抗肿瘤效力均优于传统小分子顺铂药物. 该研究对于纳米颗粒靶向药物控释与肿瘤治疗具有启发意义.

2019年，Cunningham等[105]采用水溶性PEG化钌卡宾催化剂(PEG-G3)，以聚乙二醇功能化聚降冰片烯(NB-PEG)作为大分子引发剂、1,5-环辛二烯(COD)作为成核单体，通过ROMPISA合成了稳定的纳米乳胶(图10). NB-PEG大分子引发剂上的PEG侧链为颗粒提供了稳定作用，在NB-PEG=30 mol%、COD=70 mol%时获得了直径约200 nm的纳米乳胶，为开发无表面活性剂的稳定乳胶体系提供了借鉴.

3 水/有机相开环易位聚合诱导自组装

水溶性Grubbs催化剂的出现，实现了水相ROMP以及ROMPISA. 然而，水溶性催化剂的合成相对困难，由于较低的引发效率导致水相体系ROMP产物分子量和分子量分布的可控性较差[106]. 针对上述问题，提出了基于商品化Grubbs G3催化剂的水/有机混合溶剂作为介质的ROMPISA策略,首先在与水互溶的有机溶剂中合成亲水性大分子引发剂，然后加入亲水性单体的酸性水溶液进行扩链. 在此过程中，酸性环境的引入是保障聚合顺利进行的关键要素，一方面促进G3催化剂中吡啶配体的快速解离，另一方面有效抑制了水相环境中OH^-亲核进攻导致的催化剂失活，提高了聚合体系的稳定性，保障了分子

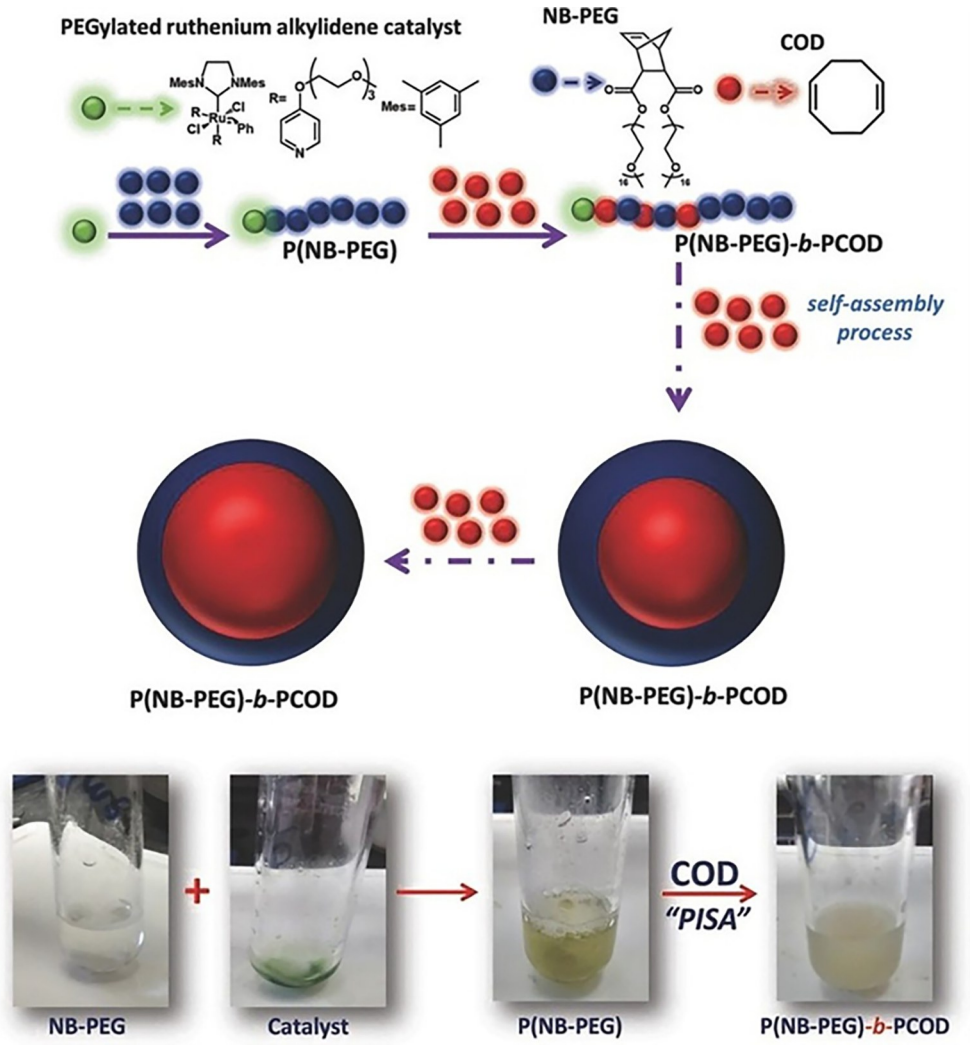

Fig. 10 General approach for ring-opening metathesis polymerization (ROMP) of cyclic olefins in aqueous media *via* polymerization-induced self-assembly (PISA) (Reprinted with permission from Ref. [105]; Copyright (2018) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

量及分子量分布的优异可控性[107]，实现了水/有机相开环易位聚合诱导自组装.

2018年，O'Reilly等[108]在THF中利用G3催化叔胺功能化降冰片烯(M1)聚合制备了大分子引发剂，加入水溶性降冰片烯衍生物M2 (成核单体)的磷酸缓冲溶液，实现了水/有机相ROMPISA (图11，Route 2). 在THF/磷酸缓冲溶液中，大分子引发剂中的侧链叔胺基团经质子化由疏水转变

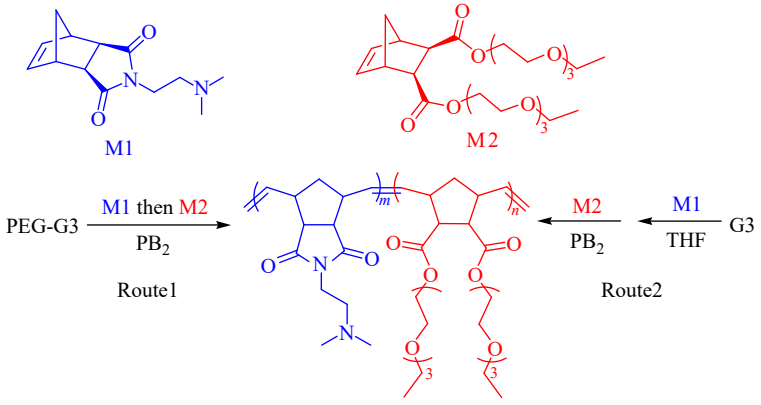

Fig. 11 Schematic of two strategies for aqueous ROMP.

为亲水[109]，酸性环境赋予了G3催化ROMPISA过程良好的可控性，嵌段共聚物分子量为6.2k~21.8k Da、多分散系数$Đ$小于1.35. 传统方法中(图11 Route 1)需要合成水溶性PEG-G3催化剂，聚合产物的多分散系数$Đ$大于2.0.

2019年，O'Reilly等提出基于低聚物亲/疏水性(LogP_{oct}/SA)参数模型，评估不同结构单体在水/有机相ROMPISA中作为亲溶剂嵌段或成核嵌段的适用性(图12(a))，拓展了单体范围[110]. 该模型有效预测PISA过程中的自组装行为，随着疏水嵌段聚合度(DP)和单体LogP_{oct}/SA提高，纳米颗粒形貌能够从球形向蠕虫及囊泡结构演变(图12(b)). 通过在降冰片烯中引入不同的锚定基团和末端基团，改变单体的亲/疏水性，实现对纳米颗粒形貌的调控. 该工作验证了模型的有效性，为单体设计赋予纳米颗粒更多功能提供了理论依据.

同年，O'Reilly等利用ROMPISA过程中产生的内在膜张力，驱动了聚合物囊泡的自发融合，在无外力作用下制备了管状的纳米囊泡(图13)[111].

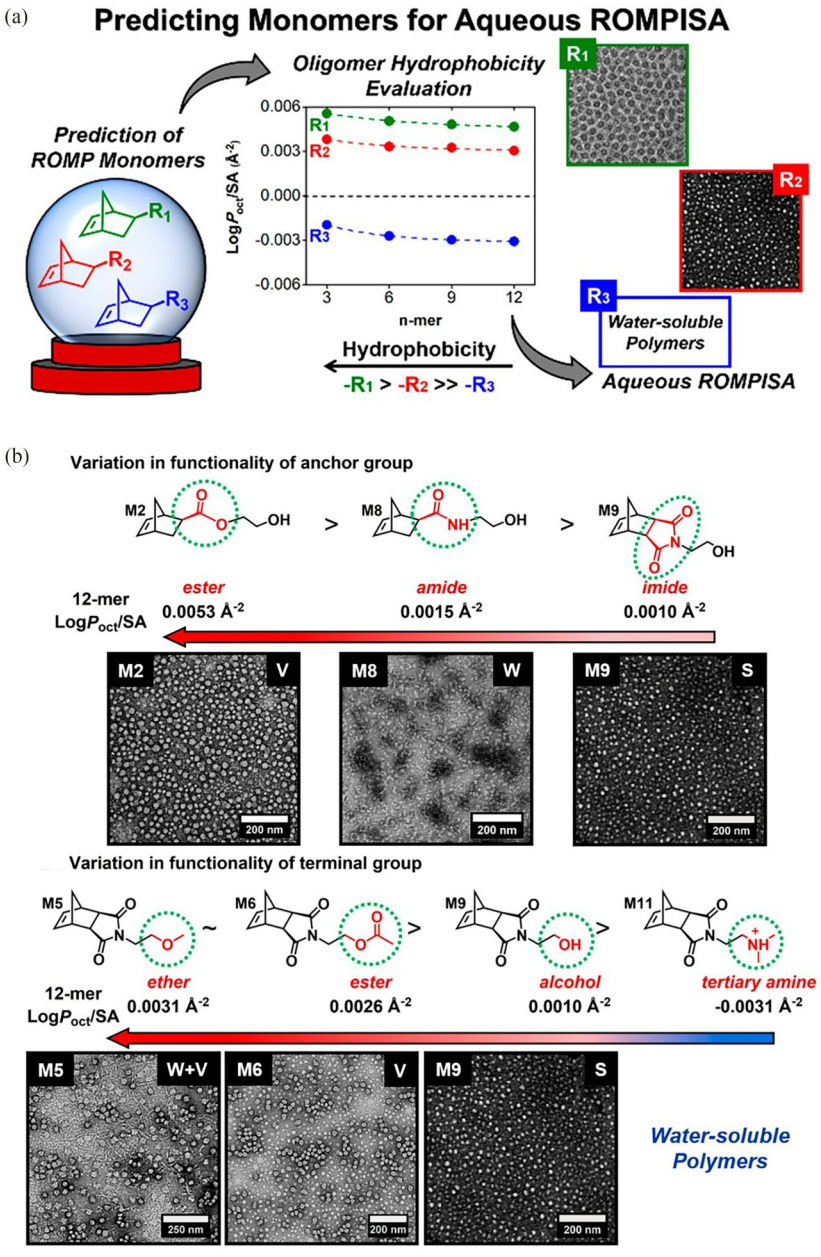

Fig. 12 (a) LogP_{oct}/SA-based hydrophilicity/hydrophobicity model; (b) LogP_{oct}/SA analysis of norbornene monomers shows hydrophobicity trends for anchor and terminal groups (Reprinted with permission from Ref. [110]; Copyright (2018) American Chemical Society).

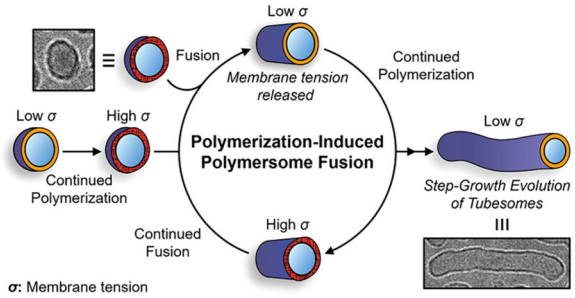

Fig. 13 Mechanism of polymerization-induced polymersome fusion (Reprinted with permission from Ref. [111]; Copyright (2018) American Chemical Society).

利用G3催化剂在四氢呋喃(THF)中分别催化亲水单体氨基降冰片烯(NB-amine)和聚乙二醇降冰片烯(NB-PEG)聚合，得到2种水溶性大分子引发剂，加入甲基乙二醇降冰片烯(NB-MEG)的PB缓冲液，探索了水/有机相ROMPISA. 相比于受静电排斥作用维持球形的阳离子型P(NB-amine)囊泡，电中性的P(NB-PEG)壳层通过消除静电势垒，促进了囊泡间的接触与融合. 筛选P(NB-PEG)作为亲溶剂大分子引发剂，随着成核嵌段聚合度的增加，膜内张力逐渐累积，当超过临界阈值时，足以克服能量壁垒，驱动相邻球形囊泡发生自发融合释放能量，形成管状结构. 为验证这一机理，采用福斯特共振能量转移(FRET)技术，将供体(ACM)和受体(RhB)探针引入到壳层与核层的界面处，观测到了伴随囊泡融合产生的特征能量转移信号，确证了融合过程的发生. 共聚焦显微镜观察到FAM/Cy5双标记囊泡腔内的染料共定位现象，进一步验证了腔室融合. 该融合现象遵循独特的类逐步聚合模型，未来有望为智能纳米反应器、多药物协同递送以及复杂人工细胞器的开发提供新的材料设计思路.

4 结论与展望

开环易位聚合诱导自组装(ROMPISA)已成为聚合诱导自组装领域的重要分支，具有可控性好、官能团耐受性高、反应条件温和、适配大位阻单体等优势，高效获得了一系列含不饱和双键聚烯烃嵌段共聚物的纳米颗粒，固含量高，形貌多样，呈现出有趣的功能以及广阔的潜在应用前景. 展望未来，开环易位聚合诱导自组装挑战与机遇并存，建议关注以下方向：(1) 形貌方面，通过ROMPISA尽管已经制备出球形、蠕虫、囊泡3种基本形貌以及纳米毛虫等特殊形貌，但是在高级形貌发现、颗粒均一性提高以及形貌可控演化等方面的研究仍然比较薄弱，亟待从催化剂、反应介质等角度深入理解ROMP聚合动力学，结合人工智能和过程强化等技术手段，发展纳米颗粒形貌调控的理论模型和实验策略. (2) 功能方面，已报道ROMPISA纳米颗粒的功能存在局限性，应充分利用颗粒中的不饱和双键进行化学修饰，将环境敏感、力场响应、动态共价键等结构单元引入到大分子引发剂或单体，将ROMP与ATRP、RAFT、ROP等可控聚合耦合，赋予纳米颗粒不同的结构与多样化功能；(3) 应用方面，合成工作仍然占据了ROMPISA研究的主要精力，仅有部分案例开展了在生物医学、催化等方面的初步探索，多数纳米颗粒的应用前景尚不明晰，建议加强以不同应用目标为导向的协同创新，指导纳米颗粒的形貌设计与功能调控，充分挖掘ROMPISA的潜力与价值，促进相关领域快速发展.

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Review

Ring-opening Metathesis Polymerization-induced Self-assembly

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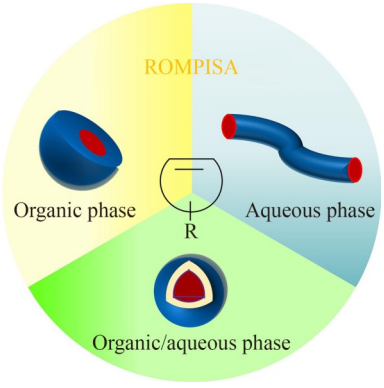
Abstract Polymerization-induced self-assembly (PISA) has emerged as a highly efficient strategy for the synthesis of high-solid-content nano-objects with diverse morphologies, which has attracted growing interest in polymer chemistry and nanomaterials. In recent years, the ring-opening metathesis polymerization (ROMP) of cyclic olefin monomers has been used in PISA because of its good controllability, high tolerance for functional groups, and availability for sterically hindered monomers. Ring-opening metathesis polymerization-induced self-assembly (ROMPISA) has been demonstrated as a powerful platform for the preparation of a series of polyolefin block copolymer nano-objects containing unsaturated double bonds in the main chain. This review focuses on the advances in ring-opening metathesis polymerization-induced self-assembly. The morphologies, functions, and applications of nano-objects from ROMPISA are summarized from the perspectives of the organic, aqueous, and organic/aqueous phases, respectively. Challenges and opportunities are discussed to provide insights into the further development of polymerization-induced self-assembly.



Keywords Ring-opening metathesis polymerization; Polymerization-induced self-assembly; Block copolymer; Nano-object

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