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基于脂肪族聚酯的形状记忆材料

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摘要 形状记忆高分子材料是一种能记住变形前形状，并在一定环境刺激下得到回复的智能材料．其独特的性质使其可以应用于生物医用、电线电缆、汽车工业、航空航天等领域．脂肪族聚酯以其优异的生物相容性、生物降解性，以及适合的热转变温度范围，在具有形状记忆功能的生物医用材料的设计开发中扮演着越来越重要的角色．本文重点介绍了以聚乳酸(PLA)、聚对二氧环己酮(PPDO)、聚丁二酸丁二醇酯(PBS)、聚十五烷酸酯(PPDL)和聚己内酯(PCL)等为基本组成链段，以物理交联和化学交联为网点结构的脂肪族聚酯共聚物、交联网络及互穿网络在形状记忆材料设计中的应用，阐述了链段拓扑结构对形状记忆行为的影响．

关键词 脂肪族聚酯，形状记忆材料，嵌段共聚物，交联网络，互穿网络

作为一种刺激响应型智能材料，形状记忆高分子(shape memory polymers, SMPs)是指具有一定初始形状的制品，在一定条件下改变其初始形状并固定，受到外界刺激后又可回复到其初始形状的高分子材料．与其他形状记忆材料如形状记忆合金和陶瓷相比，SMPs具有密度小、形变大、结构易调控及性能多样性等优点，已被成功应用于生物医用材料、电缆护套、纺织工业、汽车工业及航空航天等领域[1~8]．

从材料结构上来看，SMPs通常由两部分组成：控制临时形状的分子开关(molecular switch)和记忆永久形状的网点(netpionts)．可用于分子开关的结构包括了聚合物的可逆相转变、超分子相互作用、光响应基团等多种类型，而这些多样性的结构赋予了SMPs的多种刺激响应特性，如热刺激(包括直接热刺激[9~11]和由光、电或磁场作用下通过能量转化产生的间接热刺激[12~17])、光刺激(光异构化或光可逆反应)[18~20]、化学因素(湿气、溶剂、pH或者其他化学因素)[21~24]等．其中，直接热刺激响应型SMPs最为常见，聚合物的熔点(T_m)、玻璃化转变温度(T_g)或液晶相转变温度(T_{cl})均可作为形状记忆材料的转变温度(T_{trans})．可充当网点的结构包括物理交联结构、化学交联结构、互穿网络结构和超分子网络结构等．

近年来，随着对SMPs的深入研究以及需求的多样化，其结构已从最简单体系向复杂体系发展，而材料功能也向着多种刺激响应、多重形状记忆以及多功能化等方向发展．随着生物降解材料的发展，研究开发可生物降解的SMPs成为新的研究热点．具有优异生物降解性、生物相容性和生物可吸收性的脂肪族聚酯，如聚乳酸(PLA)、聚乙醇酸(PGA)、聚对二氧环己酮(PPDO)、聚十五烷酸酯(PPDL)、聚丁二酸丁二醇酯(PBS)、聚己内酯(PCL)和聚羟基烷酸酯(PHA)等成为制备具有形状记忆功能的生物材料的重要选择．上述聚酯大部分为结晶聚合物，具有良好的结晶能力并具有不同的T_m范围(表1)，因此既可利用其链段结晶形成的物理交联点作为SMPs网点，又可利用其结晶熔融的可逆转变作为SMPs分子开关，其T_m可充

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表 1　不同脂肪族聚酯的T_m及T_g

Table 1　T_m and T_g range for different aliphatic polyesters

脂肪族聚酯	T_m(℃)	T_g(℃)	参考文献
聚(L-乳酸)PLLA	174	61	[25]
PDLLA	–	54	[26]
PGA	220	45	[27]
PPDO	110	–15~–8	[28]
PPDL	97	–27	[29]
PBS	116	–37	[25]
PCL	60	–60	[25]
PHA(PHBv)$^{a)}$	161	0	[30]

a) PHBv，聚羟基丁酸戊酸共聚酯

当T_{trans}. 此外，一些无定型聚酯如聚(D,L-乳酸)(PDLLA)，PGA共聚物的T_g也可充当T_{trans}. 结合其本身结构性能特点，本文主要介绍了以结晶性脂肪族聚酯或聚醚酯为基本组成链段所构筑的具有不同网点结构的可生物降解SMPs.

1　形状记忆脂肪族聚酯共聚物

在SMPs结构设计中，具有两相结构的线形多嵌段共聚物以其合成简便、热塑性易加工等优点备受青睐，其中具有良好结晶能力的脂肪族聚酯在SMPs的设计中得到了广泛应用. 2002年，Lendlein[31]报道了以PPDO为硬段、PCL为软段的形状记忆自缩紧手术缝合线. 通过调节链段的长度和比例可以获得优异的形状记忆性能，其形状固定率(R_f)高达98%，形状回复率(R_r)值会随着循环次数的增加而渐渐地趋于100%. 图1很好地展示了样品在40℃时的回复过程及材料应用于手术缝合线的自缩紧过程. 波兰的Scandola课题组[32]以PLA，PGA，聚三亚甲基碳酸酯(PTMC)为共聚单元合成的三元共聚物显示出良好的形状记忆行为. 景瑕斌、陈学思课题组[33~35]以及王身国课题组[36,37]也设计了一系列基于PLA, PGA, PPDO和PCL的共聚体系，并考察了其形状记忆行为，获得良好效果. 周绍兵课题组[38]报道了一种基于PCL和PDLLA共聚物的形状记忆支架材料.

本课题组[39~41]利用PPDO，PBS和PCL等脂肪族聚酯与脂肪族聚醚聚乙二醇(PEG)、聚四氢呋喃(PTMEG)设计合成了一系列基于可生物降解聚酯的嵌段共聚(醚)酯. 如以PPDO为硬段、PEMEG为软段的PPDO-PTMEG多嵌段共聚醚酯[39]，利用PTMEG链段的结晶温度和PPDO链段的T_g十分接近的特点，使PTMEG链段的晶区和处于玻璃态的PPDO链段无定型区都起到了固定临时形状的作用，PPDO链段结晶形成的物理交联则起到记忆永久形状的作用. 研究发现，选择在高于或低于PPDO链段T_g的温度下进行材料临时形状固定，其R_f分别为69%和92%，进一步证实了该作用机理(图2). 这种设计使得材料在PPDO链段的含量很高(85%，质量分数)的情况下仍具有很好的形状记忆性能，同时保证材料优异的力学性能. 此外，L929细胞培养实验结果表明，PPDO-PTMEG多嵌段共聚醚酯具有高于空白对照的细胞存活率，具有良好的生物相容性.

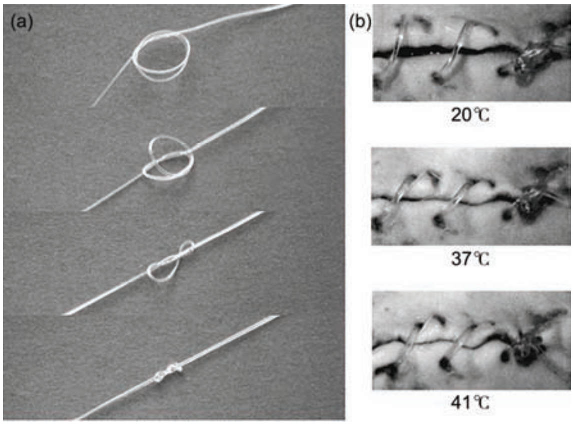

图 1　(a) PPDO-PCL多嵌段共聚物样品拉伸到200%并且打上一个结在40℃下20 s的回复过程; (b) PPDO-PCL多嵌段共聚物样品作为缝合线在动物伤口上在体温附近的收缩回复过程[31]

Figure 1　(a) The 20 s recovery process of PPDO-PCL multiblock copolymers samples under 40°C after being stretched to 200% and got a knot. (b) The shrinking recovery process of PPDO-PCL fiber in an animal would around body temperature[31]

与传统的聚氨酯(PU)合成方法类似，上述多嵌段共聚酯多采用异氰酸酯扩链制得，这需要对异氰酸酯加入量进行精确控制. 最近，本课题组[40,41]报道了一种采用丁二酸、丁二醇和双端羟基PEG通过直接酯化和缩合制备以PBS为硬段、PEG为软段的PBSEG

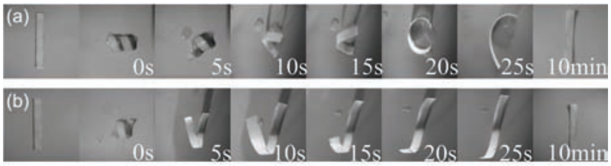

图 2　多嵌段共聚物PPDO$_{9.9}$-PTMEG$_{2.9}$-85/15 分别在–20℃(a)和–6.5℃(b)固定温度下固定后的回复过程照片[39]

Figure 2　The recovery process of PPDO$_{9.9}$-PTMEG$_{2.9}$-85/15 at –20°C (a) and –6.5°C (b), respectively[39]

多嵌段共聚物的简便方法．研究表明[42,43]，PBS和PEG链段在无定形态是相容的，PBSEG多嵌段共聚的也只显示出一个居于两种聚合物之间的T_g．由于PBS和PEG均为结晶性很强的聚合物，在较宽的共聚组成范围内，PBSEG多嵌段共聚物的DSC曲线均显示出2个很强的分别对应于PBS和PEG链段的结晶峰和熔融峰．系统的结晶行为研究证明，PBS和PEG晶区呈现微相分离结构[44~46]．形状记忆研究显示PBSEG具有优异形状记忆性能，R_f和R_r值都在96%以上．该材料不仅具有非常优异的韧性，同时通过改变PEG链段的分子量，可以调节形状记忆材料的T_{trans}，实现材料在37℃下的形状记忆回复，使其在生物医用材料领域有着良好的应用前景．

在此基础上，通过在PBSEG多嵌段共聚物中添加导电介质碳纳米管(CNTs)，实现了材料的电致响应性[41]．在材料制备过程中，采用原位聚合的方法使CNTs在基体中达到良好的分散状态，当其添加量为0.5%(质量分数)时，便能形成导电逾渗网络(图3(a), (b))．研究还发现，通过引入CNTs不仅促进了复合材料中PBS和PEG链段的结晶，改善了材料形状记忆性能，还起到了增强作用，使复合材料的屈服强度和杨氏模量明显增加．与直接热刺激响应的SMPs相比，该电致响应形状记忆复合材料还具有远程控制、过程控制和区域控制的优势(图3(c), (d))．

总体而言，具有两相结构的形状记忆脂肪族聚酯共聚物具有分子结构易调控、热塑性加工方便等优点．实际上，这一类SMPs是通过共聚物中热转变温度较低链段的结晶或玻璃化转变来实现对形状的固定，因此通常情况下提高软段的分子量和含量有利于提高材料的R_f[47]．另一方面，SMPs通过共聚物中热转变温度较高的链段结晶所形成的物理交联来实现对初始形状的记忆，只有共聚物中硬段含量必须占到一定比例，才能保证其结晶度达到理想的程度，以确保材料的R_r达到应用要求，这对于需要引入2个或以上分子开关的多重形状记忆高分子(MSPs)的设计带来一定的困难．另外，通过结晶形成的物理交联点不如通过化学交联网络的交联强度高，如果从初始形状到临时形状的改变需要通过大形变和大应力来实现时，这种物理交联结构容易发生链段的滑移，使得材料的回复性能受到影响．

2 形状记忆脂肪族聚酯交联网络

化学交联网络在SMPs的结构设计中占有非常重要的地位．不同于嵌段共聚物，交联网络的拓扑结构和交联程度对材料的形状记忆性能有重要的影响．Behl和Lendlein[48]将在SMPs广泛采用的化学交联网络归纳为以下几种(图4)：(1) 直接将分子开关链段通过网点连接形成的单一交联网络；(2) 由一种聚合物

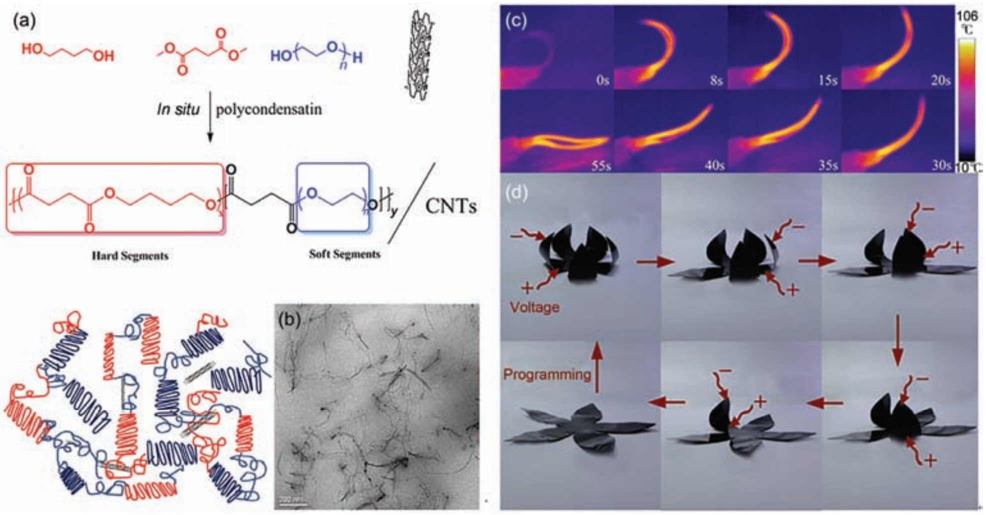

图 3 (网络版彩色)(a) PBSEG/CNTs复合材料的制备; (b) $PBSEG_{10K-39}/CNT_{0.5}$透射电子显微镜照片; (c) $PBSEG_{10K-38}/CNT_{1.0}$样片在60 V电压下的回复红外摄像照片过程; (d) $PBSEG_{10K-39}/CNT_{0.5}$花瓣状样片局部形状记忆回复过程[41]

Figure 3 (Color online) (a) Preparation scheme of PBSEG/CNTs nanocomposites. (b) Transmission electron microscope (TEM) images of $PBSEG_{10K-39}/CNT_{0.5}$. (c) The electro-induced recovery process of $PBSEG_{10K-38}/CNT_{1.0}$ under 60 V recorded by infrared thermal video camera. (d) The local shape recovery process of a flower-shape film of $PBSEG_{10K-39}/CNT_{0.5}$[41]

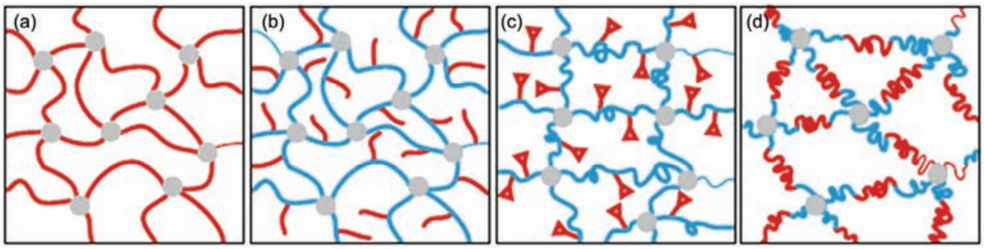

图 4 (网络版彩色)不同化学交联网络结构示意图. (a) 单一组分交联网络结构; (b) 侧链充当分子开关的网络结构; (c) 侧基可以形成可逆结构的网络结构; (d) ABA三嵌段共聚物交联形成网点的网络结构[48]

Figure 4 (Color online) (a) Switching segments linking netpoints; (b) side chains as switching segments; (c) functional groups as molecular switches capable to reversibly form a covalent bond; (d) ABA triblock segments linking netpoints[48]

交联网络构成网点，该聚合物主链上的悬垂链段充当分子开关; (3) 由一种聚合物交联网络构成网点，其侧基上具有可形成可逆的共价键的官能团充当分子开关; (4) 由ABA三嵌段共聚物交联形成的网络结构.

化学交联网络结构的多样性为其在MSPs中的应用提供了多种选择. Lendlein课题组[49,50]报道了以端羟基的星形四臂PCL预聚物、星形三臂PPDL预聚物为前驱体，二异氰酸酯为交联剂制备出具有三重形状记忆的交联网络. 其中，PPDL和PCL链段分别为2个可逆转变相，其T_m相差至少在20°C以上，可以充当2个独立的T_{trans}. 由于将2种聚合物链段共聚到一个网络中，其结晶行为受到相互影响. 通过调节2个链段的长短和比例，可以实现对共聚网络结构的优化. Lendlein课题组[10,51]还设计合成了一种由PCL链段交联形成网络、PEG以侧链形式连接在PCL链段上的CLEG网络结构，该材料显示了优异的三重形状记忆性能(图5). 他们还合成了一种基于PCL和聚(环己基甲基丙烯酸)(PCHMA)的AB型共聚网络，该网络可以通过一步程序实现三重形状记忆行为[52]. 周绍兵课题组[53]将肉桂酸基团分别修饰到星形PCL和线性PEG的链端，采用光交联方式制备了三重形状记忆共聚网络[53]. 本课题组[54]用星形三臂PPDO预聚物和线性PEG为前驱体制备了共聚交联网络，通过调节PPDO和PEG链段的长度和比例，实现材料三重形状记忆效应.

前面介绍的形状记忆网络基本是基于非动态共价键交联形成的，这种网络结构的缺点就是不能重复加工，限制了其应用范围. 近年来，利用动态共价键或非共价键来构筑可逆交联网络成为高分子材料的一个重要发展方向. 在保证其形状记忆功能的同时，可赋予材料可重复加工性能或自修复功能. 本课题组[55]利用Diels-Alder(D-A)反应制备了可逆PPDO-PTMEG交联网络，该网络不仅具有三重形状记忆功能，同时还具有可反复成型加工和自修复功能，制备路线如图6(a)所示. D-A反应是一个含双烯分子和一

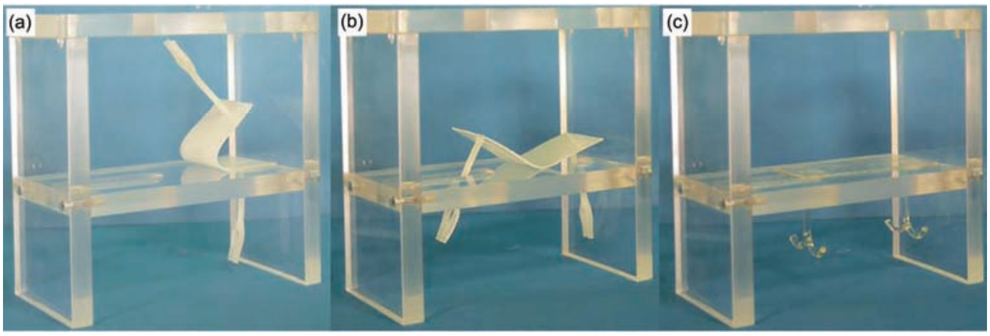

图 5 (网络版彩色)CL(50)EG样片三重形状记忆的回复过程照片. (a) 室温下的临时形状A; (b) T_{mid}下的第 2 个临时形状B; (c) T_{high}下的永久形状[10]

Figure 5 (Color online) Series of photographs illustrating the triple-shape effect of a fastener device prepared from CL(50)EG consisting of a plate with anchors as demonstration object. (a) Temporary shape A at room-temperature; (b) second temporary shape B around T_{mid}; (c) permanent shape C at T_{high}[10]

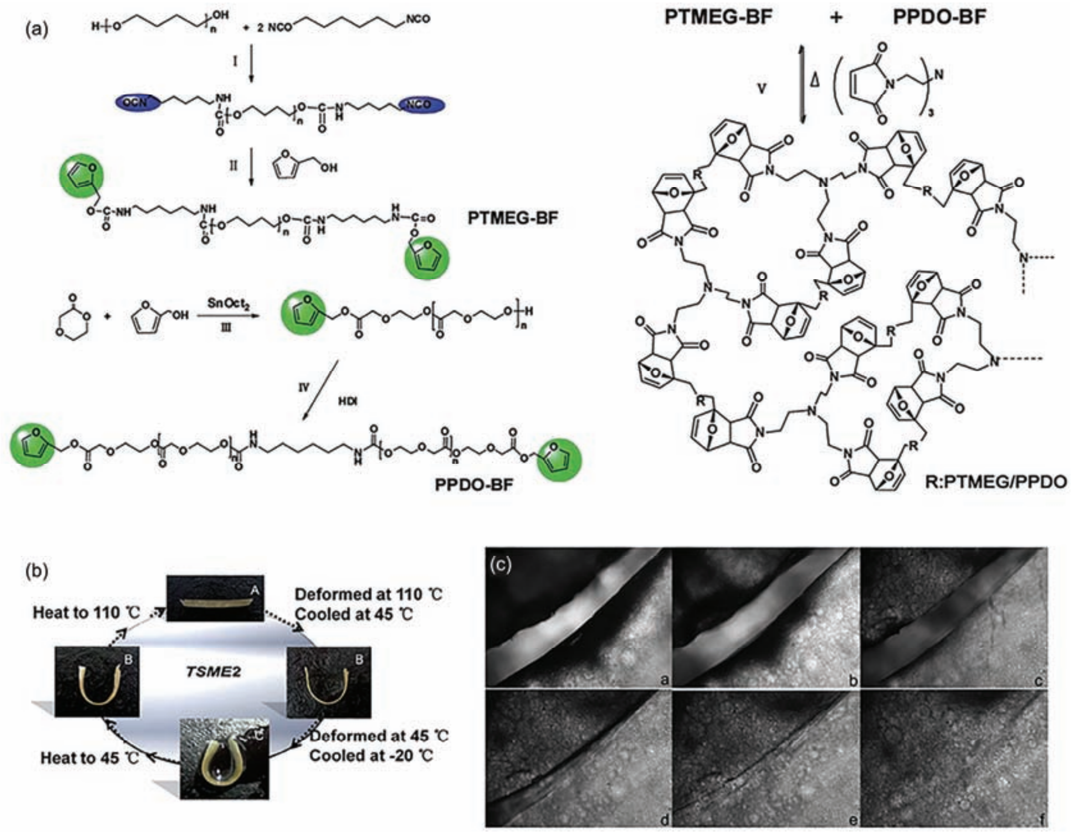

图 6 (网络版彩色)(a) PPDO-BF、PTMEG-BF和PPDO-PTMEG动态交联网络的制备以及结构示意图. PPDO-PTMEG可逆交联结构材料的三重形状记忆过程(b)和修复记录照片(c)[55]

Figure 6 (Color online) (a) The preparation and structures of PPDO-BF, PTMEG-BF and PPDO-PTMEG co-networks. The triple-shape memory process (b) and self-healing (c) images of PPDO-PTMEG co-networks[55]

个亲双烯分子间的反应, 通常反应在70℃左右进行, 而在120~150℃会发生其逆反应. 因此, 通过在线性的PPDO和PTMEG的预聚物两端都修饰上呋喃环, 采用三(2-马来酰亚胺乙基)胺为交联剂在75℃利用D-A反应可获得可逆交联网络. 通过对一次加工成型以及回收再加工成型的样品进行三重形状记忆效应测试, 显示回收再加工样品性能并没有受到影响(图6(b)). 根据D-A反应及D-A逆反应发生的温度制定了合理的温度程序, 对预先破坏的样品进行修复试验. 结果显示, 材料可以得到很好地修复, 通过光学显微镜下观察可以发现样品缺口经修复后已基本愈合(图6(c)), 修复效率为75.3%. 与动态共价键相比, 基于超分子相互作用的动态非共价键具有更加温和的反应条件和优异的环境响应性受到研究人员的青睐, 利用氢键、金属-配体络合作用、π-π堆砌、主客体相互作用等来构筑动态交联网络给SMPs的设计带来新的思路. 本课题组[56]通过将2-脲基-4[1H]-嘧啶酮(UPy)基团引入到星形四臂PCL和线形PTMEG预聚物的链端, 利用Upy基团之间自识别形成四重氢键的特点, 成功制备出通过非共价键交联的PCL-PTMEG动态交联网络, 该材料同样具有优异三重形状记忆功能和自修复能力, 其修复条件更加温和(图7).

但是, 在上述体系中由于氢键的键能相对共价键而言较低, 而且预聚物分子量不高, 所以所制备的交联网络的力学性能较差. 由于金属-配体络合作用在超分子相互作用中结合能较高, 因此本课题组[57]利用Fe(Ⅱ)与联二吡啶双齿配体之间配位相互作用设计制备了形状记忆性能和力学性能都十分优异的PPDO动态交联网络(图8). 首先以含联二吡啶双齿配体二醇化合物bpy(CH_2OH)$_2$作为引发剂引发PDO单体开环聚合, 成功将配体基团引入聚合物链段, 进一步采用六亚甲基二异氰酸酯(HDI)作为偶联剂将预聚物扩链, 得到具有多个配体单元的长链聚合物(Mbpy-PPDO). 最后, 将其与金属离子Fe(II)盐进行配位得

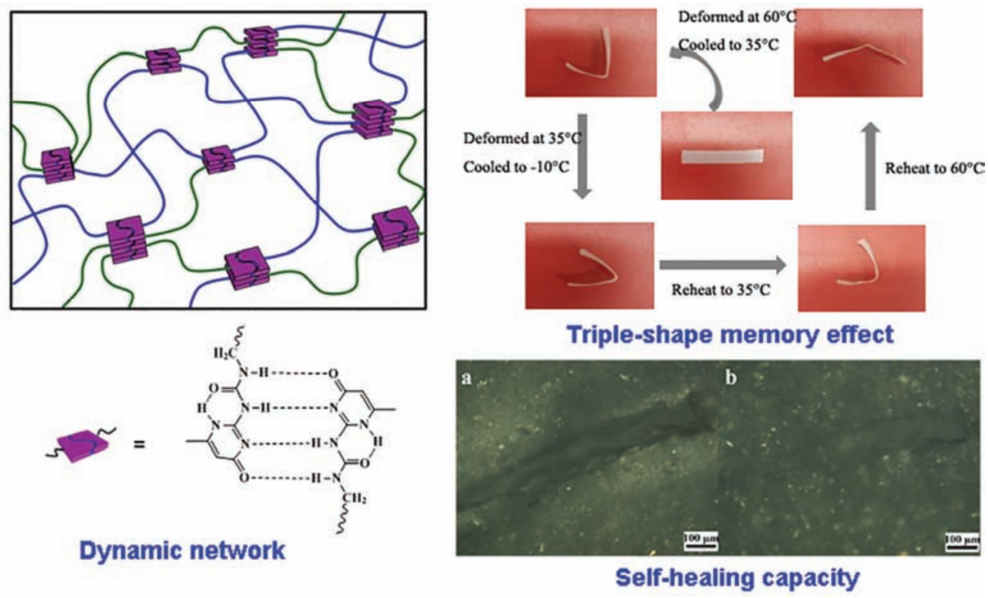

图 7 (网络版彩色)PCL-PTMEG动态交联网络的制备及其三重形状记忆性能和自修复行为[56]

Figure 7 (Color online) The preparation of PCL-PTMEG dynamic network and its triple-shape memory and self-healing effects[56]

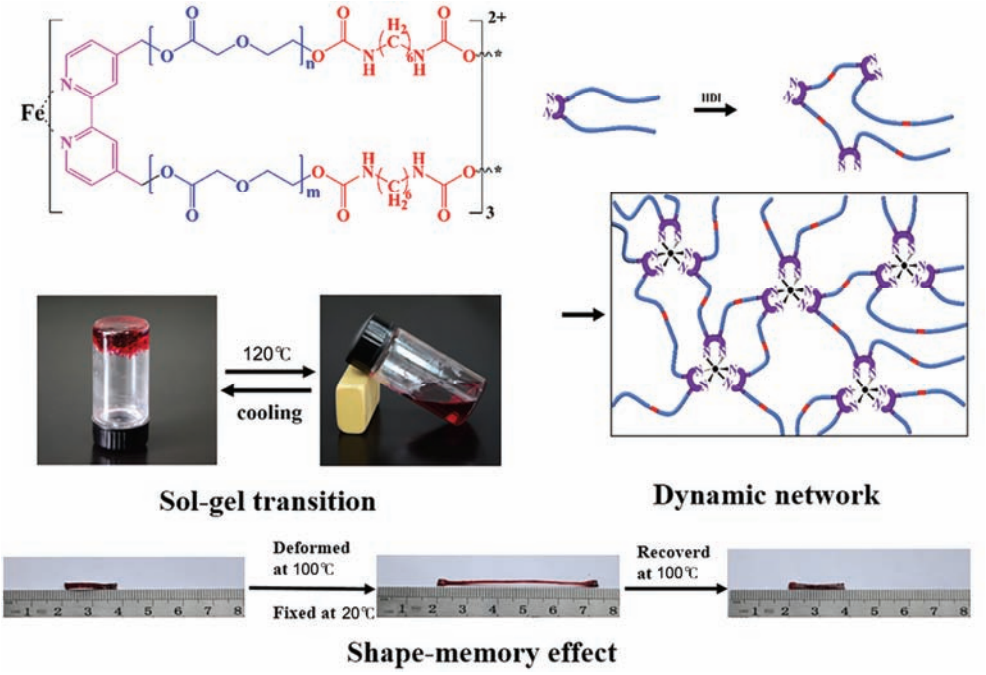

图 8 (网络版彩色)MBpyPPDO-Fe动态交联网络的制备、溶胶-凝胶转变及其形状记忆性能[57].

Figure 8 (Color online) The preparation of MBpyPPDO-Fe dynamic network, sol-gel transition and its shape-memory effects[57]

到动态网络(MbpyPPDO-Fe). 通过该合成方法得到交联网络其拉伸强度达到55 MPa, 而断裂伸长率超过800%.

前面介绍的是一些具有单程形状记忆效应(one-way SMEs)的脂肪族聚酯交联网络. 我们知道, 具有双程形状记忆效应(two-way SMEs)的SMPs最开始发展于液晶聚合物[58], 而半结晶聚合物交联网络在恒定外力条件下表现出结晶诱导增长以及熔融诱导收缩的现象[59], 也被成功应用到双程SMPs的设计中, 其中利用半结晶脂肪族聚酯PCL的研究十分活跃.

如Mather课题组[60]和Pandini等人[61]先后设计合成了基于PCL交联网络，获得了材料的两重形状two-way SMEs. Lendlein课题组[50]在PCL网络中引入了另一种脂肪族聚酯PPDL链段，得到PCL-PPDL的共聚网络，在恒定外力条件下凭借PCL，PPDL链段的应力诱导结晶，实现了材料的三重形状two-way SMEs. 冷劲松课题组[62]以PCL交联网络为基体，引入负载有Fe_3O_4纳米颗粒的多壁碳纳米管(Fe_3O_4@C)，则可得到同时具有多刺激响应和two-way SMEs的形状记忆复合材料. 上述基于PCL交联网络需要在恒定的外力条件下实现two-way SME，这极大地限制了材料的应用，因此在无外力条件下实现two-way SME成为新的研究焦点. Lendlein课题组[63]设计的PCL-PPDL交联网络，通过先将温度升到PBS和PCL熔点之上进行拉伸取向，然后再降温到两个链段的熔点之下，完成了对骨架材料内应力的预储存. 此时，控制温度程序让PCL链段结晶与熔融，材料在无外力条件下实现了two-way SME. 周绍兵课题组[64]以多臂PEG-OH引发CL开环，通过末端偶联获得的交联网络有着较宽的熔融峰，因此利用该较宽熔融峰，设计部分结晶链段在特定温度下熔融，当该部分链段再次结晶时会沿着未熔融结晶链段方向而结晶，从而获得无外力条件下的two-way SME. Anthamatten课题组[65]则通过先将PCL链段部分交联，然后在拉伸应力作用下进行二次交联的方法，将内应力预先储存在交联网络中. 由此PCL链段结晶时，分子链沿着内应力方向取向结晶，从而达到无外力条件下的双向形状记忆行为.

3 形状记忆脂肪族聚酯互穿网络

化学交联网络在三重或多重形状记忆材料中的得到了良好的应用，但是将2个及以上的聚合物链段共聚到一个网络中，链段规整性及运动能力降低导致各组分的结晶能力下降，进而影响聚合物形变的固定和回复. 如何克服因为交联和共聚对聚合物链段结晶带来的影响？近年来，互穿网络结构受到了研究人员的关注. 互穿网络聚合物(IPNs)是2种或2种以上的交联聚合物相互贯穿后形成的交织网络聚合物，是一种特殊形式的聚合物共混物. 各网络之间并没有化学键结合，既能有效降低各聚合物链段之间的相互影响，又能有效改善两组分之间的相容性，最终获得优异的形状记忆性能.

Mather课题组[66]以共混的方式合成了线形PCL/交联PCL半互穿网络(semi-IPN)，材料具有一定的形状记忆性能和自修复功能. 对于全互穿网络(full IPN)，因为需要2种不同的反应机理才能构筑互穿网络结构所以合成相对比较复杂，到目前为止关于full IPN在SMPs中的应用报道很少. Feng等人[67]用溶液浇铸法合成了由聚酯型聚氨酯和聚(乙二醇)二甲基丙烯酸酯(PEGDMA)网络构成的full IPNs，其中聚酯型聚氨酯网络由星形PDLLA和PCL共聚物与IPDI反应形成，而PEGDMA网络由通过光交联得到，IPNs的R_f和R_r都在93%以上.

本课题组[68]利用共价键和多重氢键形成机理的不同，通过一步法制备出形状记忆PPDO/PCL full IPNs. 以端羟基星形四臂PPDO预聚物和UPy封端星形四臂PCL预聚物为前驱体，在共溶剂中加入HDI同步形成互穿网络，其中PPDO链段羟基与HDI反应形成共价键交联网络，而PCL链段的Upy基团通过自识别形成四重氢键交联网络(图9). 与具有相同链段长度和比例的PPDO-PCL共聚交联网络相比，full IPNs中PPDO和PCL链段的相互影响降低，结晶度提高，显示出优异的三重形状记忆性能.

4 结语

经过研究人员数十年的不懈努力，SMPs已获得较大的进展. 从发展趋势来看，将基础研究与应用开发有机结合显得十分重要. 首先，从SMPs分子作用机理出发，设计更多新的分子开关，开发更多类型的刺激响应方式或多重响应体系，使其具有更广泛的环境适应性. 其次，基于传统物理交联及化学交联的网点结构的局限性日益突出，而动态化学、超分子科学的发展为其带来了新的思路和巨大的发展空间. 另外，针对不同应用需要，设计更加新颖的聚合物结构，在满足形状记忆功能的同时，赋予材料更多的功能性. 由于脂肪族聚酯具有优异的生物可降解性、生物相容性，其SMPs在生物医用材料领域的应用已受到高度重视，目前已成功应用到手术缝合线[31]、药物释放[69~73]、牙齿矫正[74]、血栓治疗[75]、组织修复或骨修复支架材料[76~78]和微创手术[79,80]等方面. 然而，随着医疗技术的发展，现有的形状记忆材料还远不能满足需要，需要研究人员灵活运用聚合物结构的设计与裁剪技术，通过不断探索开发出更具吸引力的多响应、多功能的新型SMPs，以满足更多领域对材料的更高需要.

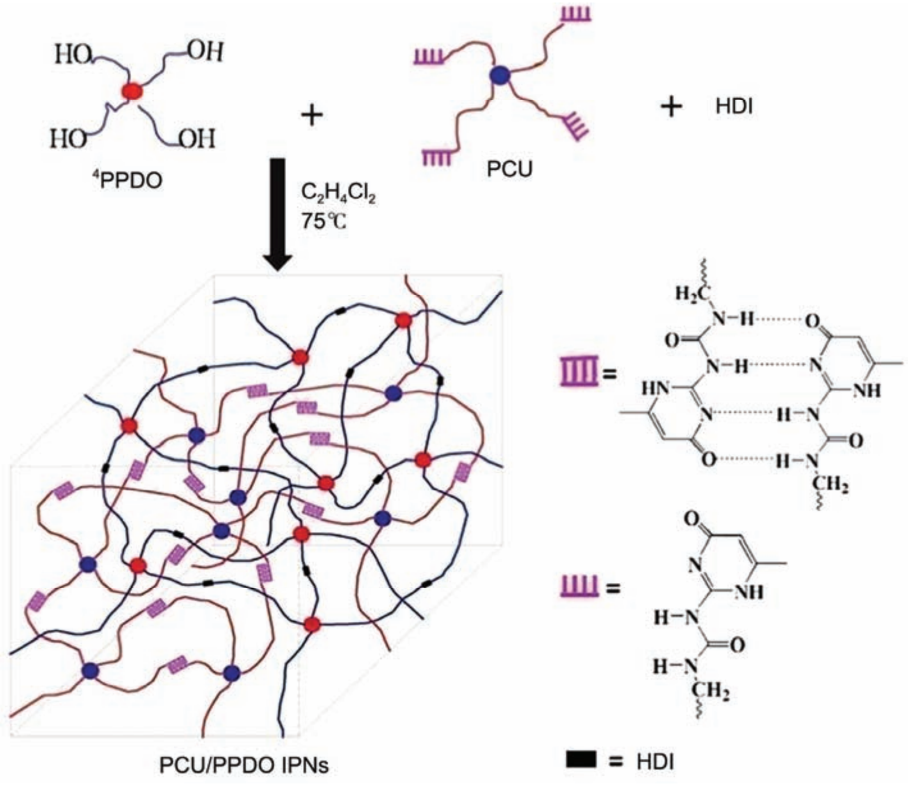

图 9 (网络版彩色)PPDO-PCU交联网络结构和互穿网络结构的制备与结构示意图[68]

Figure 9 (Color online) Synthetic approach to the PCU/PPDO IPNs[68]

参考文献

1 Huang W M, Ding Z, Wang C C, et al. Shape memory materials. Mater Today, 2010,13: 54–61

2 Behl M, Lendlein A. Shape-memory polymers. Mater Today, 2007, 10: 20–28

3 Lendlein A, Kelch S. Shape-memory polymers. Angew Chem Int Ed, 2002, 41: 2034–2057

4 Mather P T, Luo X, Rousseau I A. Shape memory polymer research. Annu Rev Mater Res, 2009, 39: 445–471

5 Liu C, Qin H, Mather P T. Review of progress in shape-memory polymers. J Mater Chem, 2007, 17: 1543–1558

6 Xie T. Recent advances in polymer shape memory. Polymer, 2011, 52: 4985–5000

7 Hu J, Zhu Y, Huang H, et al. Recent advances in shape-memory polymers: Structure, mechanism, functionality, modeling and applications. Prog Polym Sci, 2012, 37: 1720–1763

8 Leng J, Lan X, Liu Y, et al. Shape-memory polymers and their composites: Stimulus methods and applications. Prog Mater Sci, 2011, 56: 1077–1135

9 Lee K M, Knight P T, Chung T, et al. Polycaprolactone-POSS chemical/physical double networks. Macromolecules, 2008, 41: 4730–4738

10 Bellin I, Kelch S, Langer R, et al. Polymeric triple-shape materials. Proc Natl Acad Sci USA, 2006, 103: 18043–180437

11 Lee B S, Chun B C, Chung Y C, et al. Structure and thermomechanical properties of polyurethane block copolymers with shape memory effect. Macromolecules, 2001, 34: 6431–6437

12 Mohr R, Kratz K, Weigel T, et al. Initiation of shape-memory effect by inductive heating of magnetic nanoparticles in thermoplastic polymers. Proc Natl Acad Sci USA, 2006, 103: 3540–3545

13 Kumar U N, Kratz K, Wagermaier W, et al. Non-contact actuation of triple-shape effect in multiphase polymer network nanocomposites in alternating magnetic field. J Mater Chem, 2010, 20: 3404–3415

14 Xiao Y, Zhou S, Wang L, et al. Electro-active shape memory properties of poly(ε-caprolactone)/functionalized multiwalled carbon nanotube nanocomposite. ACS Appl Mater Interfaces, 2010, 2: 3506–3514

15 Lu H, Liu Y, Gou J, et al. Synergistic effect of carbon nanofiber and carbon nanopaper on shape memory polymer composite. Appl Phys Lett, 2010, 96: 084102

16 Meng Q, Hu J. A review of shape memory polymer composites and blends. Compos Pt A Appl Sci Manufact, 2009, 40: 1661–1672

17 Zhang H, Xia H, Zhao Y. Optically triggered and spatially controllable shape-memory polymer-gold nanoparticle composite materials. J Mater Chem, 2012, 22: 845–849

18 Lendlein A, Jiang H, Junger O, et al. Light-induced shape-memory polymers. Nature, 2005, 434: 876–879

19 Xie H, He M J, Deng X Y, et al. Design of poly(L-lactide)-poly(ethylene glycol) copolymer with light-induced shape-memory effect triggered by pendant anthracene groups. ACS Appl Mater Interfaces, 2016, 8: 9431–9439

20 Lee K M, Koerner H, Vaia R A, et al. Light-activated shape memory of glassy, azobenzene liquid crystalline polymer networks. Soft Matter, 2011, 7: 4318–4324

21 Yang B, Huang W M, Li C, et al. Effects of moisture on the thermomechanical properties of a polyurethane shape memory polymer. Polymer, 2006, 47: 1348–1356

22 Huang W M, Yang B, Zhao Y, et al. Thermo-moisture responsive polyurethane shape-memory polymer and composites: A review. J Mater Chem, 2010, 20: 3367

23 Kumpfer J R, Rowan S J. Thermo-, photo-, and chemo-responsive shape-memory properties from photo-cross-linked metallo-supramolecular polymers. J Am Chem Soc, 2011, 133: 12866–12874

24 Han X J, Dong Z Q, Fan M M, et al. pH-induced shape-memory polymers. Macromol Rapid Commun, 2012, 33: 1055–1060

25 Albertsson A C, Varma I K. Aliphatic polyesters: Synthesis, properties and applications. Adv Polym Sci, 2002, 157: 1–40

26 Zheng X, Zhou S, Li X, et al. Shape memory properties of poly(D,L-lactide)/hydroxyapatite composites. Biomaterials, 2006, 27: 4288–4295

27 Zong X H, Wang Z G, Hsiao B S, et al. Structure and morphology changes in absorbable poly(glycolide) and poly(glycolide-*co*-lactide) during *in vitro* degradation. Macromolecules, 1999, 32: 8107–8114

28 Yang K K, Wang X L, WangY Z. Poly(*p*-dioxanone) and its copolymers. Polym Rev, 2002, 42: 373–398

29 Focarete M L, Scandola M, Kumar A, et al. Physical characterization of poly(ω-pentadecalactone) synthesized by lipase-catalyzed ring-opening polymerization. J Polym Sci Pt B Polym Phys, 2001, 39: 1721–1801

30 Chan C H, Kammer H W. Thermal properties of blends comprising poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and epoxidized natural rubber. Polym Bull, 2009, 63: 673–686

31 Lendlein A. Biodegradable, elastic shape-memory polymers for potential biomedical applications. Science, 2002, 296: 1673–1676

32 Zini E, Scandola M, Dobrzynski P, et al. Shape memory behavior of novel (l-lactide-glycolide-trimethylene carbonate) terpolymers. Biomacromolecules, 2007, 8: 3661–3667

33 Wang W, Ping P, Chen X, et al. Shape memory effect of poly(L-lactide)-based polyurethanes with different hard segment. Polym Int, 2007, 56: 840–846

34 Ping P, Wang W, Chen X, et al. Poly(ε-caprolactone) polyurethane and its shape-memory property. Biomacromolecules, 2005, 6: 587–592

35 Wang W, Ping P, Chen X, et al. Polylactide-based polyurethane and its shape-memory behavior. Eur Polym J, 2006, 42: 1240–1249

36 Min C, Cui W, Bei J, et al. Effect of comonomer on thermal/mechanical and shape memory property of L-lactide-based shape-memory copolymers. Polym Adv Technol, 2007, 18: 299–305

37 Min C, Cui W, Bei J, et al. Biodegradable shape-memory polymer—Polylactide-*co*-poly(glycolide-*co*-caprolactone) multiblock copolymer. Polym Adv Technol, 2005, 16: 608–615

38 Yu X, Wang L, Huang M, et al. A shape memory stent of poly(ϵ-caprolactone-*co*-DL-lactide) copolymer for potential treatment of esophageal stenosis. J Mater Sci Mater Med, 2012, 23: 581–589

39 Zhang J, Wu G, Huang C, et al. Unique multifunctional thermally-induced shape memory poly(*p*-dioxanone)-poly(tetramethylene oxide)glycol multiblock copolymers based on the synergistic effect of two segments. J Phys Chem C, 2012, 116: 5835–5845

40 Huang C L, Jiao L, Zhang J J, et al. Poly(butylene succinate)-poly(ethylene glycol) multiblock copolymer: Synthesis, structure, properties and shape memory performance. Polym Chem, 2012, 3: 800–808

41 Huang C L, He M J, Huo M, et al. A facile method to produce PBS-PEG/CNTs nanocomposites with controllable electro-induced shape memory effect. Polym Chem, 2013, 4: 3987–3997

42 Qiu Z, Ikehara T, Nishi T. Miscibility and crystallization in crystalline/crystalline blends of poly(butylene succinate)/poly(ethylene oxide). Polymer, 2003, 44: 2799–2806

43 Qiu Z, Ikehara T, Nishi T. Melting behaviour of poly(butylene succinate) in miscible blends with poly(ethylene oxide). Polymer, 2003, 44: 3095–3099

44 Huang C L, Jiao L, Zeng J B, et al. Fractional crystallization and homogeneous nucleation of confined PEG microdomains in PBS-PEG multiblock copolymers. J Phys Chem B, 2013, 117: 10665–10676

45 Huang C L, Jiao L, Zeng J B, et al. Crystallization behavior and morphology of double crystalline poly(butylene succinate)-poly(ethylene glycol) multiblock copolymers. Polymer, 2012, 53: 3780–3790

46 Huang C L, Zeng J B, Jiao L, et al. Nonisothermal crystallization behaviors of biodegradable double crystalline poly(butylene succinate)-poly(ethylene glycol) multiblock copolymers. J Appl Polym Sci, 2014, 131: 40940

47 Behl M, Zotzmann J, Lendlein A. Shape-memory polymers and shape-changing polymers. Adv Polym Sci, 2010, 226: 1–40

48 Behl M, Lendlein A. Triple-shape polymers. J Mater Chem, 2010, 20: 3335–3345

49 Zotzmann J, Behl M, Feng Y, et al. Copolymer networks based on poly(*ω*-pentadecalactone) and poly(*ϵ*-caprolactone) segments as a versatile triple-shape polymer system. Adv Funct Mater, 2010, 20: 3583–3594

50 Zotzmann J, Behl M, Hofmann D, et al. Reversible triple-shape effect of polymer networks containing polypentadecalactone- and poly(*ε*-caprolactone)-segments. Adv Mater, 2010, 22: 3424–3429

51 Bellin I, Kelch S, Lendlein A. Dual-shape properties of triple-shape polymer networks with crystallizable network segments and grafted side chains. J Mater Chem, 2007, 17: 2885−2891

52 Behl M, Bellin I, Kelch S, et al. One-step process for creating triple-shape capability of AB polymer networks. Adv Funct Mater, 2009, 19: 102–108

53 Wang L, Di S, Wang W, et al. Tunable temperature memory effect of photo-cross-linked star PCL-PEG networks. Macromolecules, 2014, 47: 1828−1836

54 Niu Y, Zhang P, Zhang J, et al. Poly(*p*-dioxanone)-poly(ethylene glycol) network: Synthesis, characterization, and its shape memory effect. Polym Chem, 2012, 3: 2508–2516

55 Zhang J, Niu Y, Huang C, et al. Self-healable and recyclable triple-shape PPDO-PTMEG co-network constructed through thermoreversible Diels-Alder reaction. Polym Chem, 2012, 3: 1390−1393

56 Wei M, Zhan M, Yu D, et al. A novel poly(tetramethylene ether)glycol and poly(*ε*-caprolactone) based dynamic network via quadruple hydrogen-bonding with triple-shape effect and self-healing capacity. ACS Appl Mater Interfaces, 2015, 7: 2585–2596

57 Zhang T, Wen Z, Hui Y, et al. Facile fabrication of a well-defined poly(*p*-dioxanone) dynamic network from metallosupramolecular interactions to obtain an excellent shape-memory effect. Polym Chem 2015, 6: 4177−4184

58 Ahir S V, Tajbakhsh A R, Terentjev E M. Self-assembled shape-memory fibers of triblock liquid-crystal polymers. Adv Funct Mater, 2006, 16: 556–560

59 Chung T, Rorno-Uribe A, Mather P T. Two-way reversible shape memory in a semicrystalline network. Macromolecules, 2008, 41: 184−192

60 Lee K M, Knight P T, Chung T, et al. Polycaprolactone-POSS chemical/physical double networks. Macromolecules, 2008, 41: 4730−4738

61 Pandini S, Baldi F, Paderni K, et al. One-way and two-way shape memory behaviour of semi-crystalline networks based on sol-gel cross-linked poly(epsilon-caprolactone). Polymer, 2013, 54: 4253−4265

62 Li W B, Liu Y J, Leng J S. Shape memory polymer nanocomposite with multi-stimuli response and two-way reversible shape memory behavior. RSC Adv, 2014, 4: 61847−61854

63 Behl M, Kratz K, Zotzmann J, et al. Reversible bidirectional shape-memory polymers. Adv Mater, 2013, 25: 4466−4469

64 Gong T, Zhao K, Wang W X, et al. Thermally activated reversible shape switch of polymer particles. J Mater Chem B, 2014, 2: 6855−6866

65 Meng Y, Jiang J, Anthamatten M. Shape actuation via internal stress-induced crystallization of dual-cure networks. ACS Macro Lett, 2015, 4: 115−118

66 Rodriguez E D, Luo X, Mather P T. Linear/network poly(*ε*-caprolactone) blends exhibiting shape memory assisted self-healing (SMASH). ACS Appl Mater Interfaces, 2011, 3: 152–161

67 Feng Y, Zhao H, Jiao L, et al. Synthesis and characterization of biodegradable, amorphous, soft IPNs with shape-memory effect. Polym Adv Technol, 2012, 23: 382–388

68 Xiao L, Wei M, Zhan M, et al. Novel triple-shape PCU/PPDO interpenetrating polymer networks constructed by self-complementary quadruple hydrogen bonding and covalent bonding. Polym Chem, 2014, 5: 2231−2241

69 Wischke C, Neffe A T, Lendlein A. Controlled drug release from biodegradable shape-memory polymers. In: Lendlein A, ed. Advances in Polymer Science. Berlin, Heidelberg: Springer Berlin Heidelberg, 2009. 177–205

70 Neffe A T, Hanh B D, Steuer S, et al. Polymer networks combining controlled drug release, biodegradation, and shape memory capability. Adv Mater, 2009, 21: 3394–3398

71 Serrano M C, Carbajal L, Ameer G A. Novel biodegradable shape-memory elastomers with drug-releasing capabilities. Adv Mater, 2011, 23: 2211–2215

72 Guo X, Li D, Yang G, et al. Thermo-triggered drug release from actively targeting polymer micelles. ACS Appl Mater Interfaces, 2014, 6: 8549–8559

73 Yang G, Wang J, Wang Y, et al. An implantable active-targeting micelle-in-nanofiber device for efficient and safe cancer therapy. ACS Nano, 2015, 9: 1161–1174

74 Jung W C, Cho J W. Application of shape-memory polyurethane in othrodontic. J Mater Sci Mater Med, 2010, 21: 2881–2886

75 Langer R, Tirrell D A. Designing materials for biology and medicine. Nature, 2004, 428: 487–492

76 Huang W M, Song C L, Fu Y Q, et al. Advanced drug delivery reviews. Adv Drug Deliver Rev, 2012, 1–21

77 Small W IV, Singhal P, Wilson T S, et al. Biomedical applications of thermally activated shape memory polymers. J Mater Chem, 2010, 20: 3356–3366

78 Liu X, Zhao K, Gong T, et al. Delivery of growth factors using a smart porous nanocomposite scaffold to repair a mandibular bone defect. Biomacromolecules, 2014, 15: 1019–1030

79 Xue L, Dai S Y, Li Z. Biodegradable shape-memory block co-polymers for fast self-expandable stents. Biomaterials, 2010, 31: 8132–8140

80 Kratz K, Voigt U, Lendlein A. Temperature-memory effect of copolyesterurethanes and their application potential in minimally invasive medical technologies. Adv Funct Mater, 2012, 22: 3057–3065

Shape memory polymeric materials based on aliphatic polyesters

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Shape memory polymers (SMPs) have the capacity of memorizing a temporary shape and recovering their initial shape in response to various external stimuli. As one of promising class of intelligent materials, it has attracted great attention because of its potential applications in many areas, such as biomaterials and biotechnology, automotive industry, and aerospace field. Aliphatic polymers play an important role in the molecular design of SMPs owing to its excellent biodegradability and biocompatibility, and suitable thermal transition temperature range. This review focuses on the recent progress of shape memory polymers based on the aliphatic polyesters such as poly(lactic acid) (PLA), poly (*p*-dioxanone) (PPDO), poly(butylene succinate) (PBS), poly(ω-pentadecalactone) (PPDL) and poly(ε-caprolactone) (PCL) and so on. From the view of architecture design, different systems are classified by block copolymers, crosslinking networks and interpenetrating networks. The influence of architectural features on the shape memory behaviors is also discussed. The block copolymers have been identified a typical mature system in design of dual-shape material, and the crystalline aliphatic polyesters can be served as the netpiont or the molecular switch in a SMP, depending on its transition temperature range among the binary systems. The thermoplastic feature of block copolymers endows an easy processibility. The various architectures of crosslinking network meet the increasing demand of SMPs design. Constructing network with crystallizable polyester segment such as PCL may achieve SMPs in one-way and two-way mode, and the stress-free two-way mode can also be realized by an elaborate architecture with pre-programed treatment. Embedding two segments in one network may achieve a triple-shape memory effect, meanwhile, incorporating two segments in an interpenetrating polymer network may result in a triple-shape material with improved performance. Recently, the SMPs based on dynamic networks become the new trend, which may combine the self-healing with shape memory effect in one system, and both dynamic covalent bond and non-covalent bond have been concerned. In order to fulfill the increasing requirement of application, the SMPs with multi-shape memory effect, multi-responsibility and multi-functionality are highly expected.

aliphatic polyesters, shape-memory materials, block copolymers, crosslinking networks, interpenetrating networks

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