树形高分子：仿生合成及智能化

李文

上海大学材料学院高分子系

2012年7月5日

Content

- 有关科研论文的一些知识
- 我国高分子学科科研状况
- 树枝状大分子介绍
- 本课题组工作介绍

科研论文介绍

http://www.sciencemag.org/magazine **Science**

Top Journal!

http://www.nature.com/siteindex/index.html **Nature**

http://www.sciencedirect.com **Elsevier**出版社

http://onlinelibrary.wiley.com **Wiley**出版社

书、杂志种类很多

期刊的*影响因子*(**Impact factor，IF**)，是表征期刊影响大小的一项定量指标。

2011年IF= 2011年引用的（2009+2010年所发文章）次数/ （2009+2010年所发文章总数）

2011年各杂志影响因子

Wiley出版社

http://onlinelibrary.wiley.com

Advanced Materials 13.877
Advanced Functional Materials 10.179
Angewandte Chemie International Edition 13.455
Chemistry – An Asian Journal 4.5
Chemistry - A European Journal 5.925
Macromolecular Rapid Communications 4.596
Journal of Polymer Science Part A: Polymer Chemistry 3.919
Macromolecular Chemistry and Physics 2.361

http://pubs.acs.org/ 美国化学会(ACS)

Chemical Reviews 40.197
Journal of the American Chemical Society 9.907
Macromolecules 5.167
ACS Macro Letters—New in 2012
Biomacromolecules 5.479
Chemistry of Materials 7.286
Nano Letters 13.198
Organic Letters 5.862

http://pubs.rsc.org/en/journals 英国皇家化学会(RSC)

Chemical Society Reviews 28.76
Soft Matter (2005-Present) 4.39
Chemical Communications 6.169
Journal of Materials Chemistry (1991-Present) 5.968
Polymer Chemistry (2010-Present) 5.321(for the first year!)

文献类型

Review （综述）
Communication (快报）
Letter （快报）
Perspective (Future article, 展望）
Article （文章）

中国：
杂志分区（1, 2, 3, 4)

常用的科研信息网站（中国）

http://www.sciencenet.cn/	科学网
http://emuch.net/bbs/	小木虫
http://www.polymer.cn/	中国聚合物网

中国化学基础研究现状与地位

2009年SCI论文最多的十个学科

中国科学技术信息研究所最新发布（2010年11月26日）

排序	学科	论文数（篇） 2009	%
1	化学	28799	22.59
2	物理学	13927	10.92
3	生物	13121	10.29
4	临床医学	7014	5.50
5	材料科学	6859	5.38
6	数学	5620	4.41
7	基础医学	4878	3.83
8	电子、通讯与自动控制	4324	3.39
9	地学	3509	2.75
10	环境科学	3288	2.58

中国SCI论文共12.75万篇, (全球排列第2)化学占22.59%,

2009年高等院校国际论文

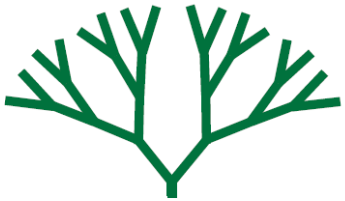
排序	单位	被引用篇数	被引用次数
1	浙江大学	3,712	11,122
2	北京大学	3.007	10,722
3	清华大学	2,746	10,038
4	上海交通大学	2,533	8,777
5	中国科技大学	2,522	9,077
6	复旦大学	2,419	9,106
7	南京大学	2,132	8,296
8	武汉大学	1,657	5,613
9	中山大学	1,397	5,338
10	山东大学	1,376	4,578

我国化学学科产出力以及影响力明显上升

- 国际1%顶尖论文分布

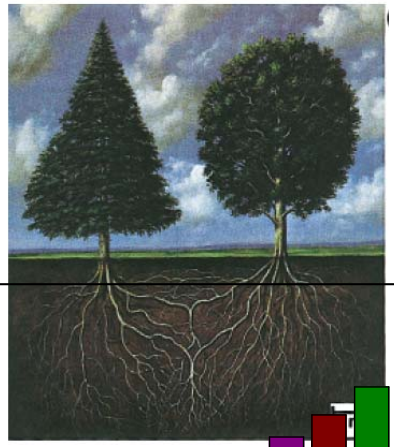
排位	1997		1998-2000		2001-2005		2006-2007	
	国别	论文数	国别	论文数	国别	论文数	国别	论文数
1	美国	470	美国	1427	美国	2667	美国	435
2	德国	86	德国	318	德国	598	德国	114
3	日本	78	日本	251	日本	440	中国	77
5					中国	275		
12			中国	49				
15	中国	9						

树枝状大分子介绍



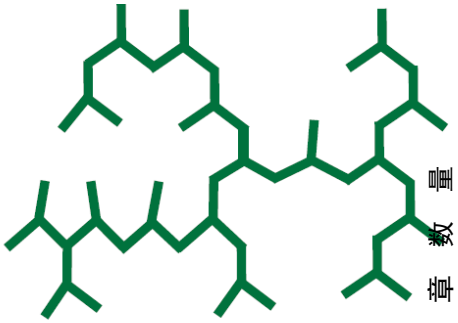
Dendron

树枝化基元



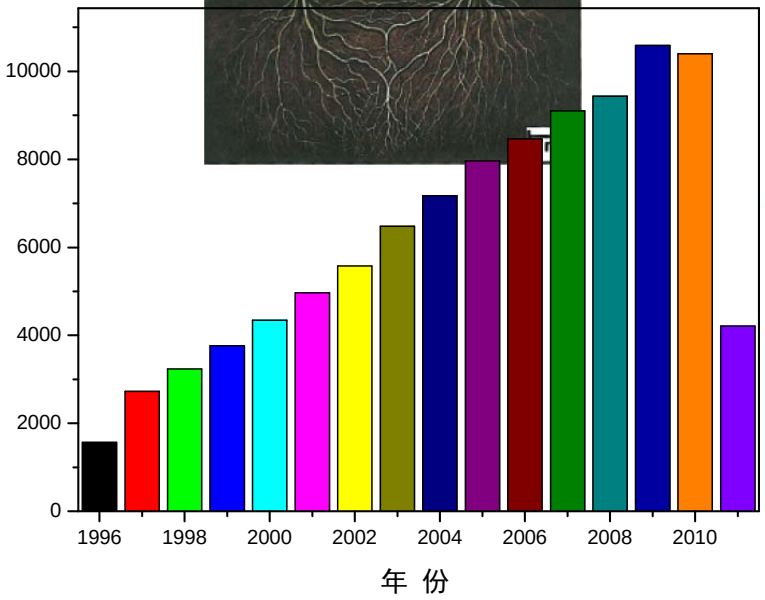
Dendrimer

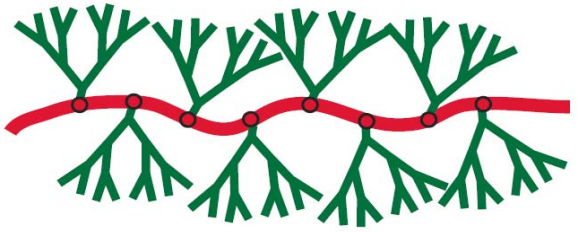
树枝状大分子



Hyperbranched polymer

超枝化聚合物





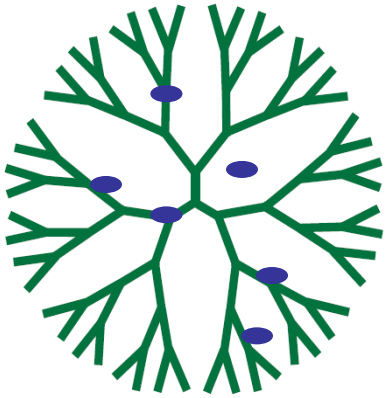
Dendronized polymer

树枝化聚合物

一代(G1)　二代(G2)　三代(G3)　四代(G4)

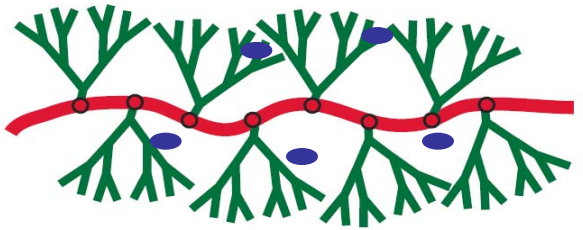
Conventional linear polymer

线形聚合物



Dendrimer

四代树枝状大分子



Dendronized polymer

三代树枝化聚合物

结构特点：高度枝化、分子尺寸可调节、内外官能团可调节

应用领域：药物传递载体、信息存储、催化、分子器件等

最早的树枝状大分子

February 1978 Communications 155

1978

收率低
提纯困难

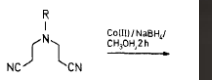
of similar steps would be advantageous. Neutral ligand syntheses carried out so far[2], have not taken due advantage of this principle. We made use of this repeating-step principle in order to annex successive arms or rings in the synthesis of noncyclic and cyclic polyaza compounds *with increasingly growing cavity size*. Starting from monoamines (Scheme **A**), diamines (Scheme **B**), or else from a diaza-monocyclic ring such as **8** and adopting the now described "cascade-like" (Schemes **A** and **B**) or "nonskid-chain-like" (Scheme **C**) pathway for bond-formation, we succeeded in synthesizing noncyclic polyaza compounds, e.g. **4**, **7** and novel multicyclic medium- or large-sized ring systems such as **11**–**15**. Owing to the particular properties of the synthesized polyamines (basicity, extreme water-solubility, salt-complexation), all the synthetic steps mentioned above

respect to those involved in the us

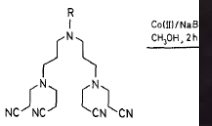
tional aza-compounds. This pa

decomplexation following the cob

tion.



1



3

Scheme A

Reaction of mono- or diamines (cf.

leads to the annexation of a pa

group[3] (compounds **1** or **5** in Schem

the nitrile groups, to amine functio

lonitrile addition yields the lengthe

3 or **7**, which upon reduction as polyamines[6] or hydrolysis as polycarboxylic acids[7] should give novel complexones.

Polycycles enlarged in the "nonskid-chain" form are obtained by reacting monocycles of type **8** with glycolic acid nitrile

D. A. Tomalia
University of Michigan, USA

"Cascade"- and "Nonskid-Chain-like" Syntheses Molecular Cavity Topologies

Egon Buhleier, Winfried Wehner, Fritz Vögtle*

Institut für Organische Chemie und Biochemie der Universität Bonn, Max-Planck-Str. 1, D-5300 Bonn

For the construction of *large* molecular cavities and pseudo-cavities that are capable of binding ionic guests or molecules (as complex or inclusion compounds) in a Host-Guest interaction[1], synthetic pathways allowing a frequent repetition

of oxygen-free hexaaza-cryptands possessing a large cavity. There is, in principle, no barrier to the annexation of more rings via the reaction sequence *a*···*d*; the chain length can be varied in the reaction step *c* (Scheme **C**).

From the synthetic point of view, it is worth noting that the smooth, glacial acetic acid-catalyzed bis-cyanoethylation of primary aliphatic oligoamines as well as the bis-cyanoethylation of bifunctional secondary amines takes place in a

0039–7881/78/0232–0155 $ 03.00

Polymer Journal, Vol. 17, No. 1, pp 117—132 (1985)

1985

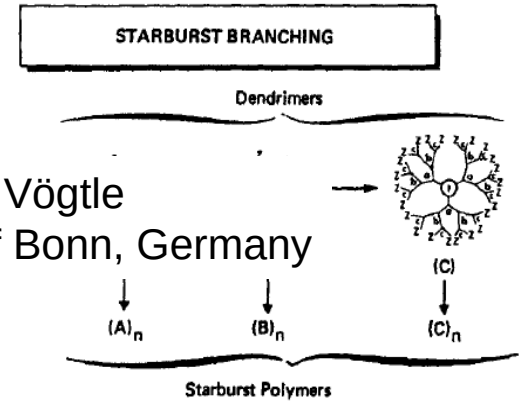
A New Class of Polymers: Starburst-Dendritic Macromolecules

D. A. Tomalia,* H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, and P. Smith

*Functional Polymers/Process and *The Analytical Laboratory, Dow Chemical U.S.A., Midland, Michigan 48640, U.S.A.*

(Received August 20, 1984)

T: This paper describes the first synthesis of a new class of topological macromol-ch we refer to as "starburst polymers." The fundamental building blocks to this new ass are referred to as "dendrimers." These dendrimers differ from classical monomers/ by their extraordinary symmetry, high branching and maximized (telechelic) terminal ty density. The dendrimers possess "reactive end groups" which allow (a) controlled weight building (monodispersity), (b) controlled branching (topology), and (c) versatility nd modification of the terminal end groups. Dendrimer synthesis is accomplished by a trategies involving "time sequenced propagation" techniques. The resulting dendrimers eometrically progressive fashion as shown: Chemically bridging these dendrimers leads class of macromolecules—"starburst polymers" (*e.g.*, $(A)_n$, $(B)_n$ or $(C)_n$).



F. Vögtle
University of Bonn, Germany

收率高
易纯化

Dendrimer Pioneers 1

D. A. Tomalia

Original Dow Dendrimer Research Team

Photo taken (1982) in Dow's Functional Polymer Research Laboratory

PAMAM dendrimer

Mw = several hundreds to over 1 million daltons

(generations 1–13)

Commercial available

发明发散法合成树枝状大分子

Dendrimer Pioneers 2

Prof. Takashi Kato
(University of Tokyo)

Dr. Craig Hawker
(IBM Laboratory)

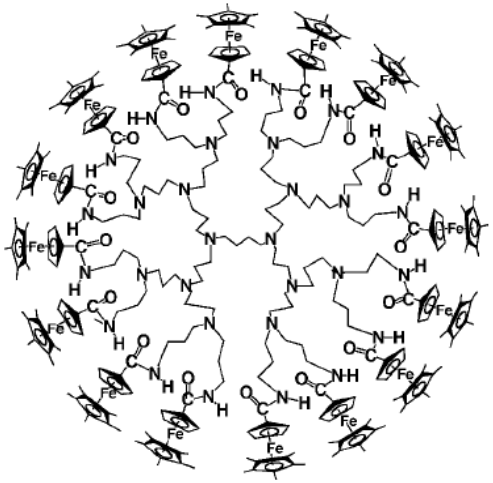
Prof. Karen Wooley
(Washington University)

Prof. Jean Fréchet
(University of California, Berkeley)

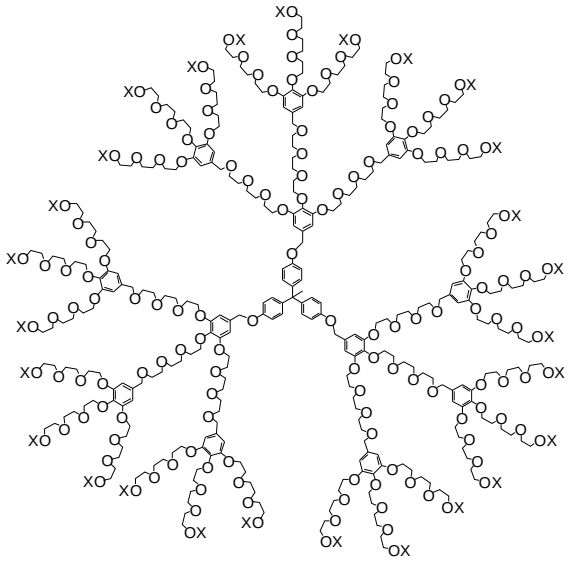
Members of the 1988–1989 Cornell University team

发明收敛法合成树枝状大分子

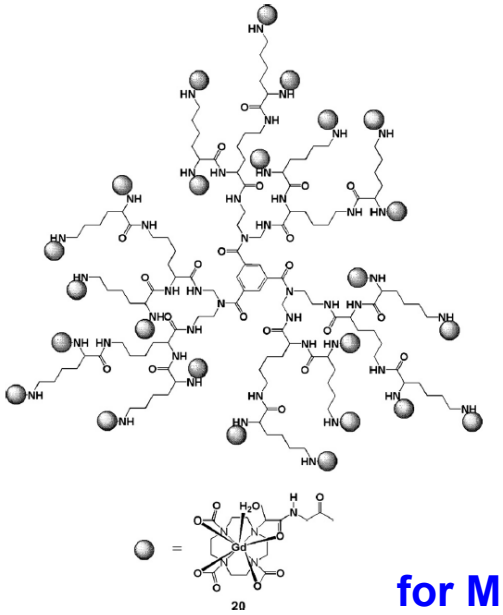
树枝状大分子的应用



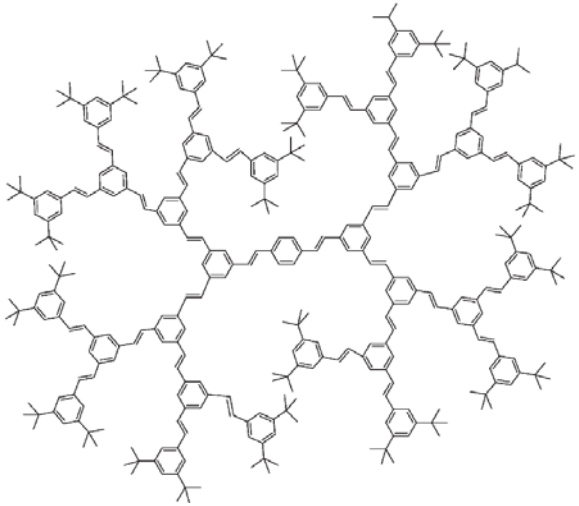
for Molecular Electronics



for drug delivery



for MRI

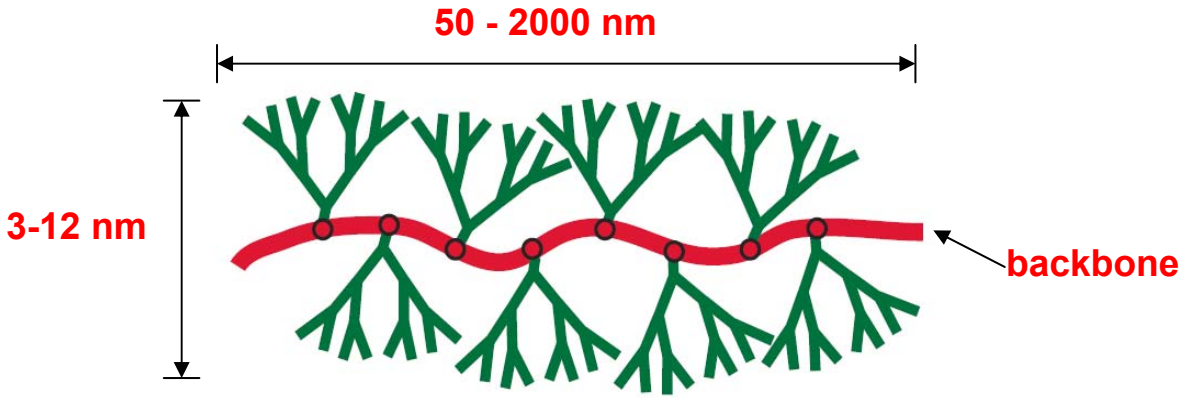


for OLED

有关树枝状大分子的书籍

树枝化聚合物

Conventional linear polymer



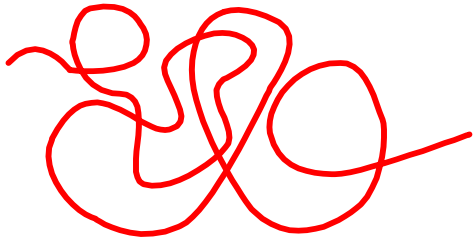
Dendronized polymer

由Prof. A. D. Schliiter于1998年命名

结构特点:

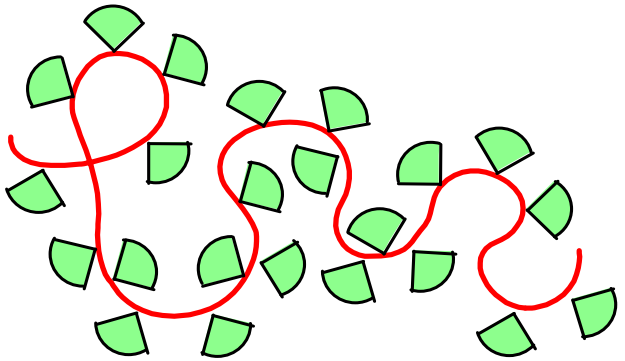
- 尺寸较大
- 厚度可调控
- 刚性较高
- 表面高密度官能团

a)



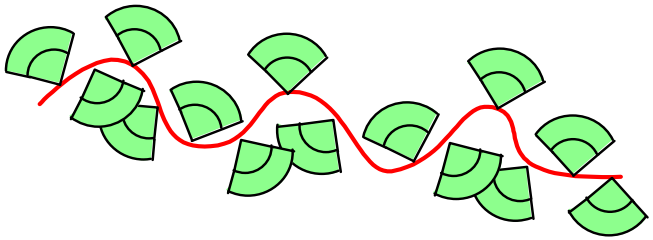
G0

b)



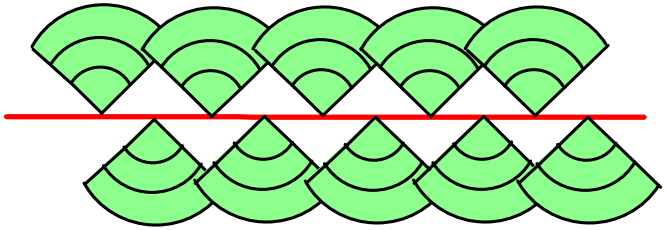
G1

c)



G2

d)

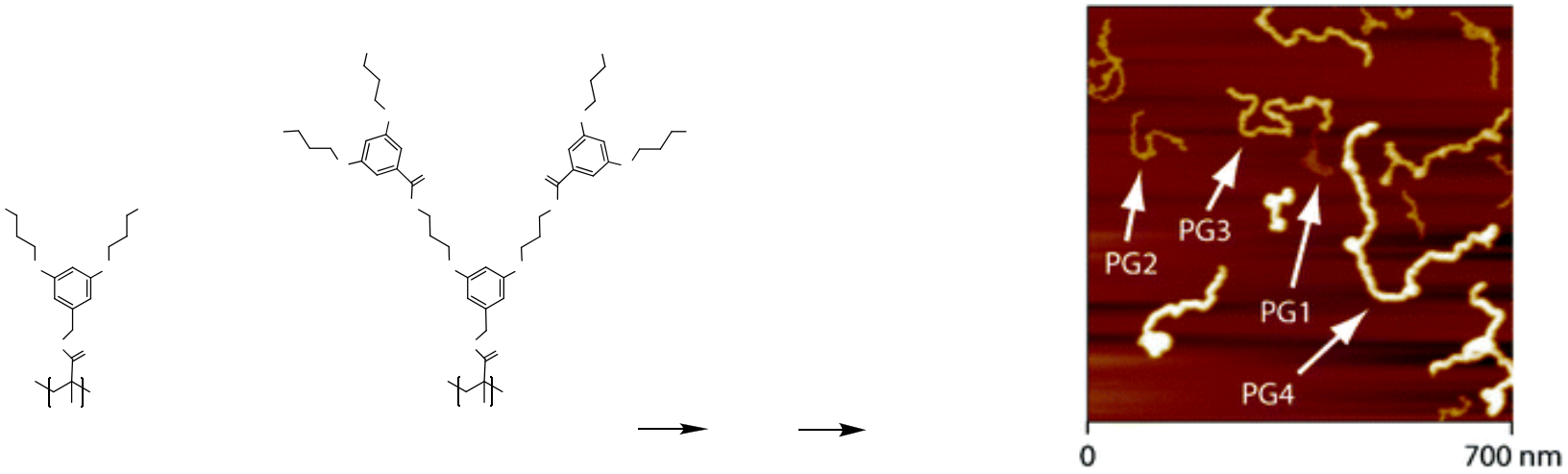


G3

随着侧基树枝化基元代数的增加，刚性逐步增大

A. Zhang, L. Shu et al. *Macromol. Chem. Phys.*, **2003**, *204*, 328

树枝化聚合物单分子形貌

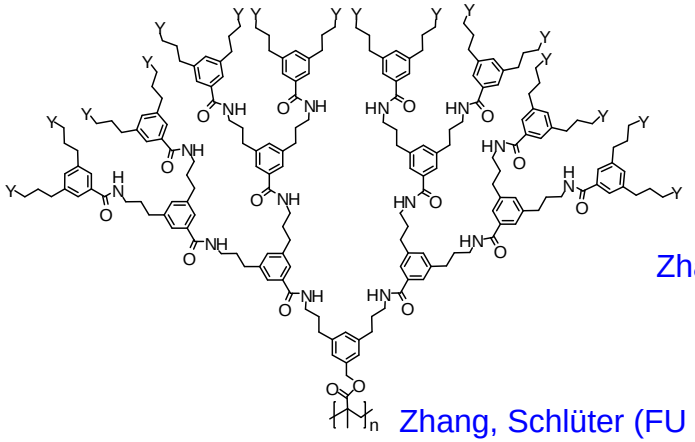


Homologous series of dendronized polymethacrylates

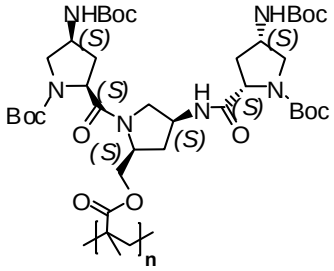
a)

Y. Guo, A. Zhang, *et al. JACS*, **2009**, *131*, 11841.

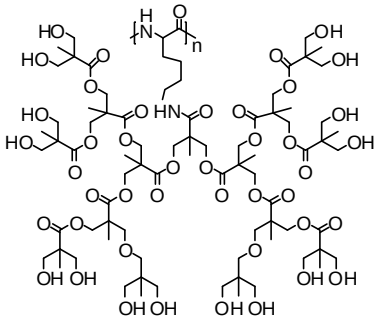
共价型树枝化聚合物



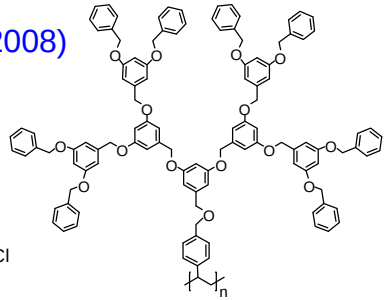
Zhang, Schlüter (FU Berlin, 2004)



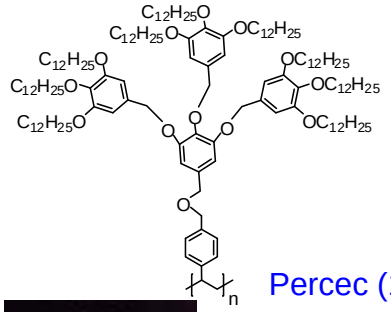
Zhang, Schlüter (FU Berlin, 2008)



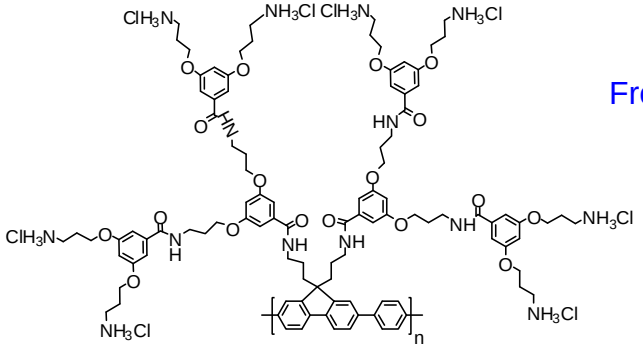
Fréchet (UC Berkeley, 2006)

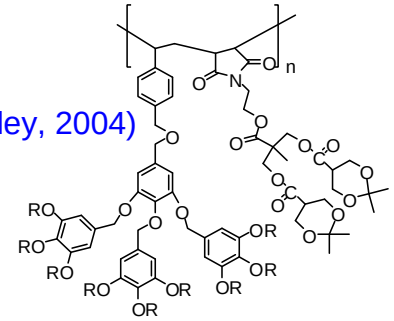


Fréchet (UC Berkeley, 2004)



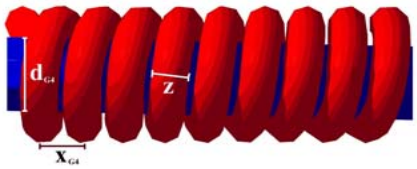
Percec (1997)





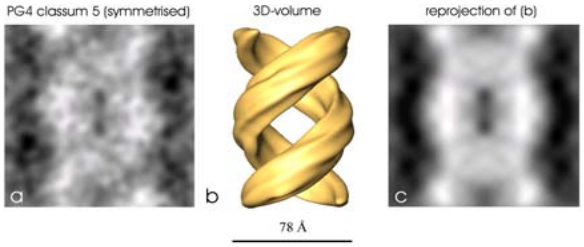
Chen, Wang (中科院北化所， 2007)

Bo (中科院北化所，2007)



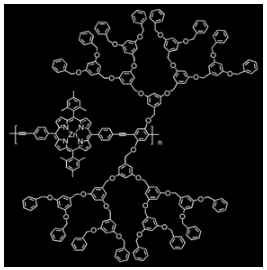
DNA wrapping

Rabe, Schlüter(2002)



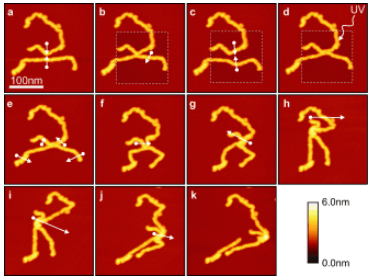
Double helices

Schlüter, Rabe (2004)



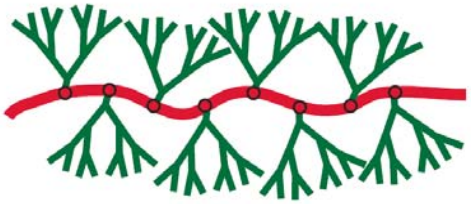
Electro-optical materials

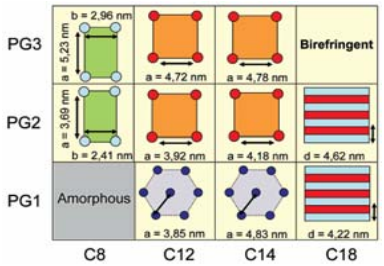
Bo (2006)



Single molecule chemistry

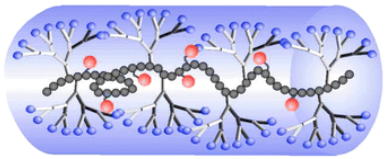
Schlüter, Rabe (2006)





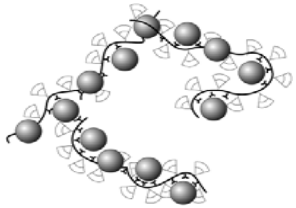
Bulk structure design

Mezzenga, Schlüter (2007)



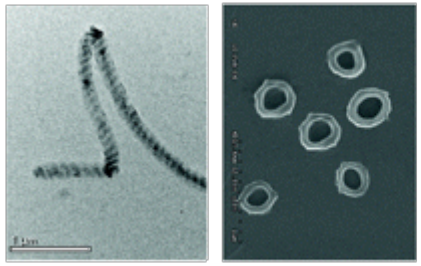
Catalysis

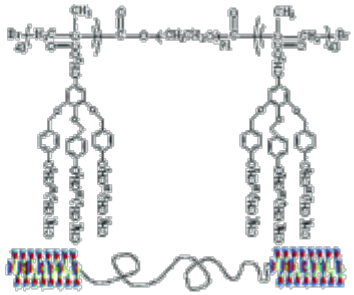
Fréchet (2004, 2006)



Nano-templates

Chen (2006)

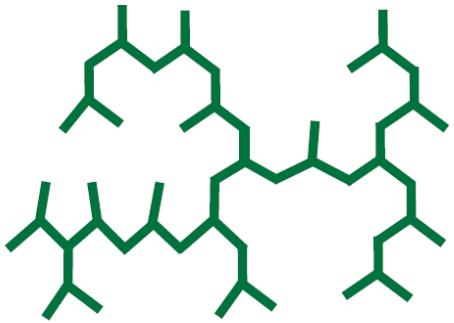




Self-assembly

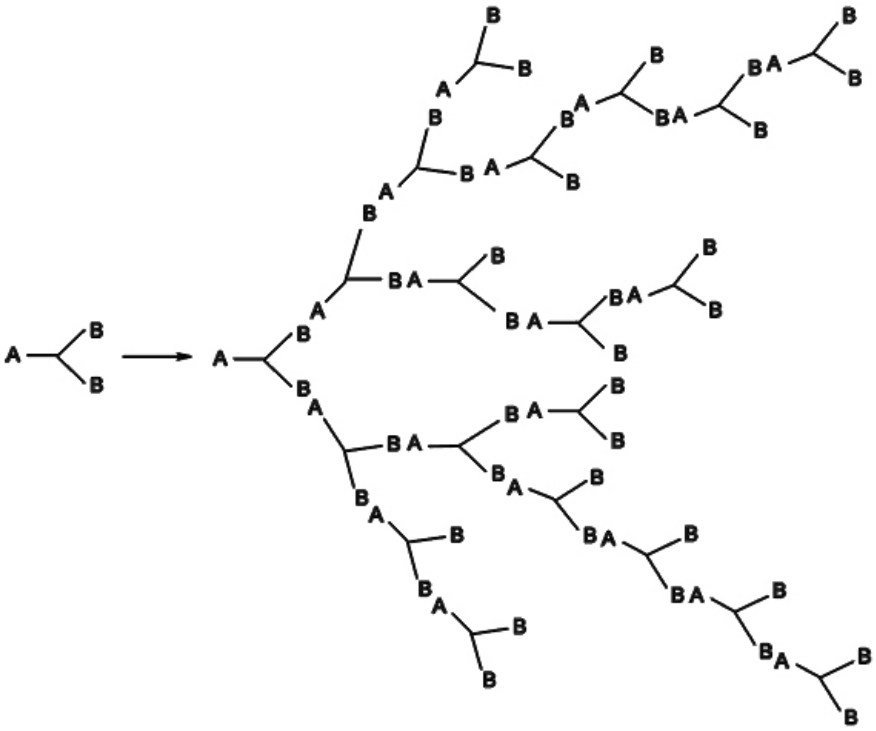
Chen, Xi (2005)

超枝化聚合物



Hyperbranched polymer

1988年，由Kim和Webster 命名



特点：

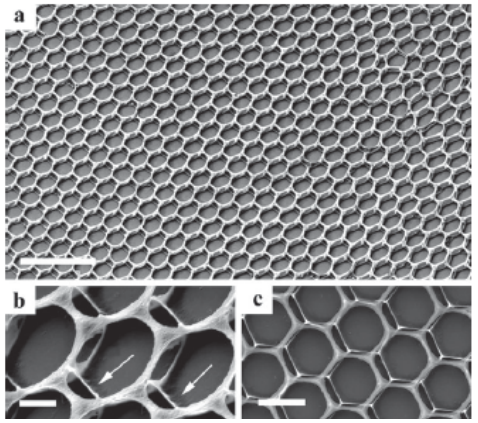
- 趋近于网状结构
- 单分子尺寸在纳米级
- 结构不完善
- 支化度不明确性
- 分子量多分散性

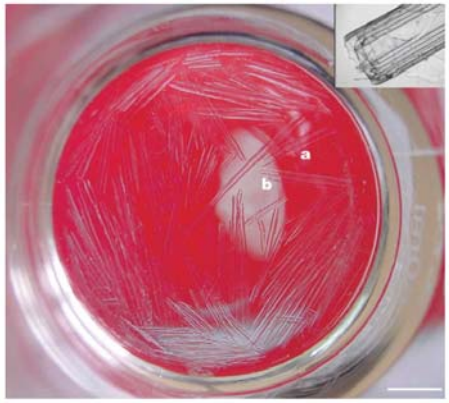
合成过程相对简单，易于工业化生产

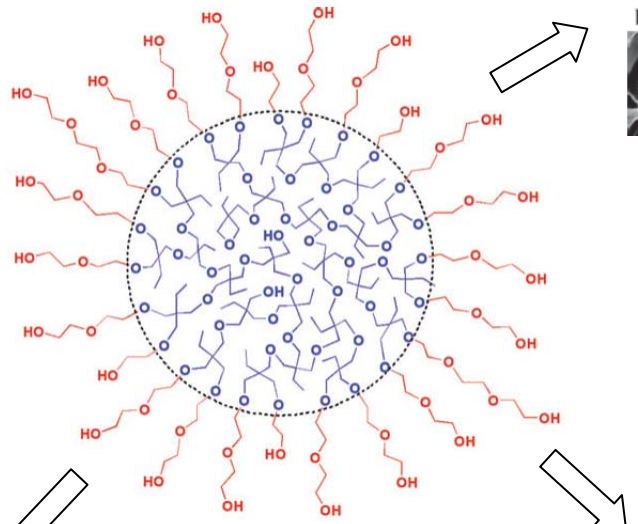
Deyue Yan

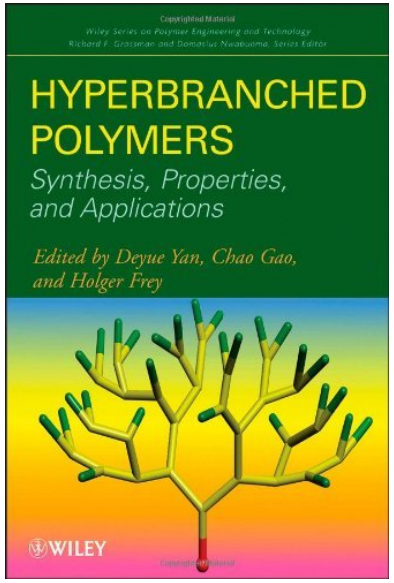
Yongfeng Zhou

上海交通大学

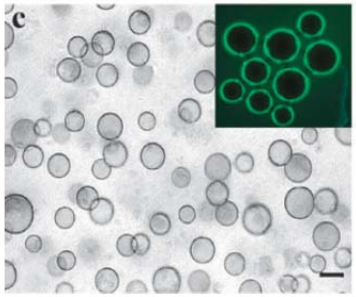


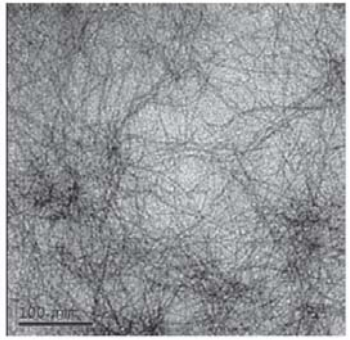






Science, 2004





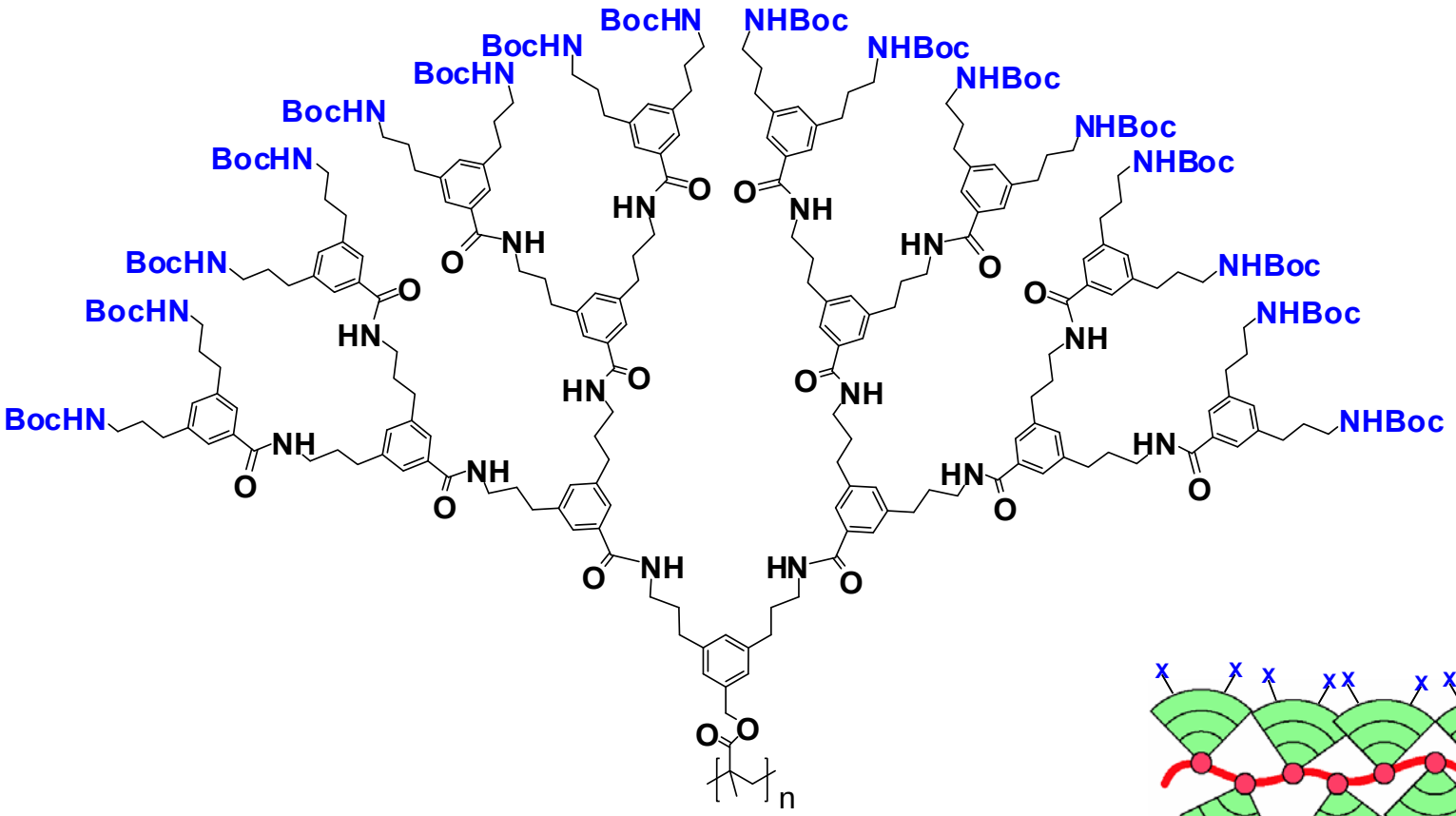
Research in our group

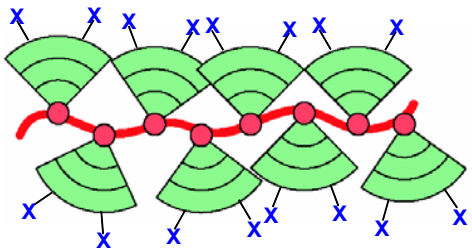
Research in Our Group

1. 大尺度仿生聚合物（树枝化聚合物、螺旋聚合物、多肽聚合物）
2. 智能聚合物材料（温敏、光敏等）

智能凝胶材料
智能有机无机杂化纳米材料
自愈合、自修复材料

早期代表性工作

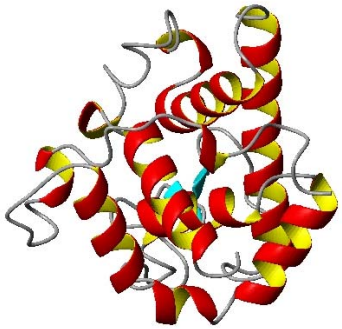




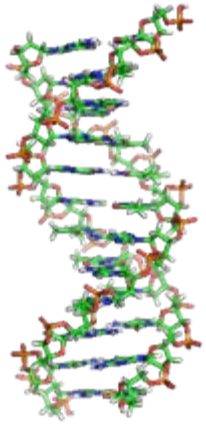
采用大单体路线成功合成了四代高分子量(几百万)树枝化聚合物

A. Zhang, *et al. Chem. Eur. J.* **2003**, *9*, 6083; A. Zhang, *et al*. *JACS* **2004**, 126, 6658.

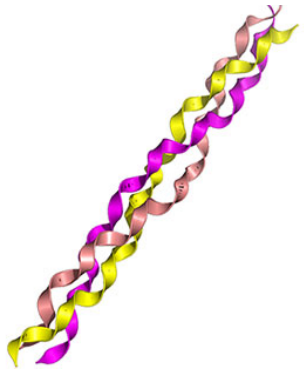
近期工作一：仿生螺旋树枝化聚合物



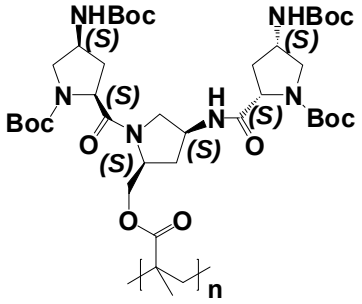
Protein, single α-helix



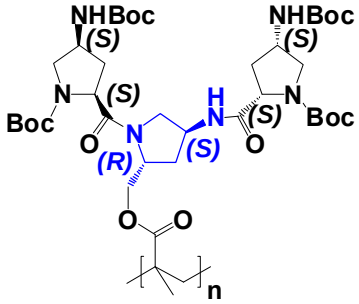
DNA, double helix



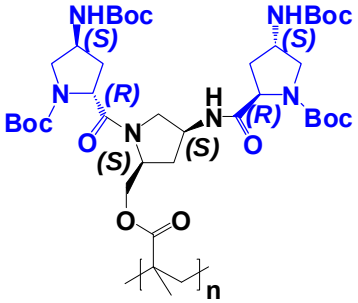
Collagen, triplex



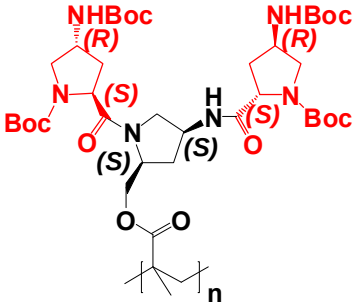
SSSS-PG2



RSSS-PG2



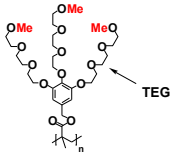
SSRS-PG2



SSSR-PG2

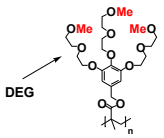
Chem. Asian J. ***2007****, 2, 1540–1548; Chem. Eur. J.* **2008**, 14, 6924– 6934;
J. Phys. Chem. B, **2009**, *113*, 14868–14876.

二、温度敏感智能树枝化聚合物（共价型）



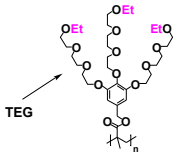
PG1(MT)

63 °C



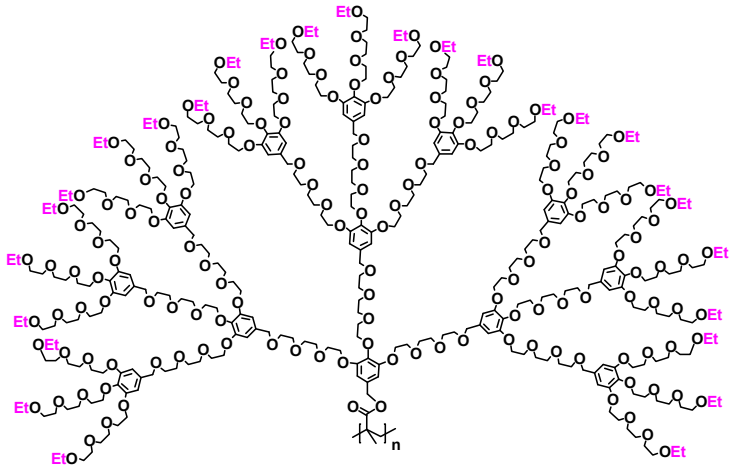
PG1(MD)

43 °C



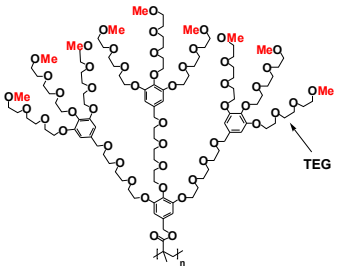
PG1(ET)

33 °C



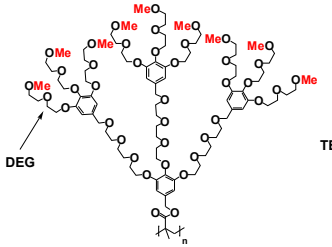
PG3(ET)

34°C



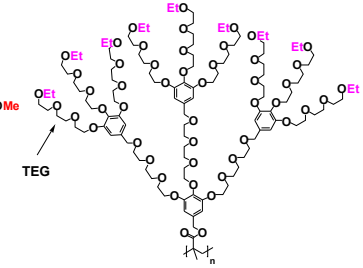
PG2(MT)

64 °C



PG2(MD)

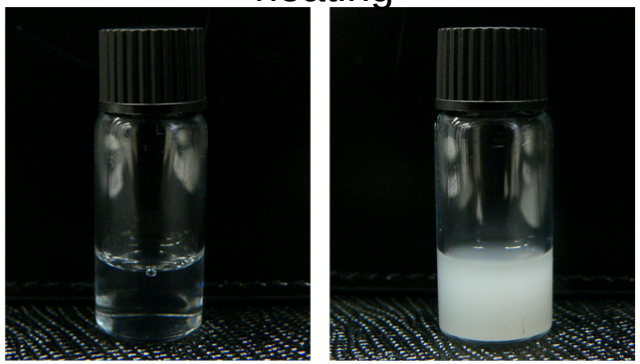
48 °C



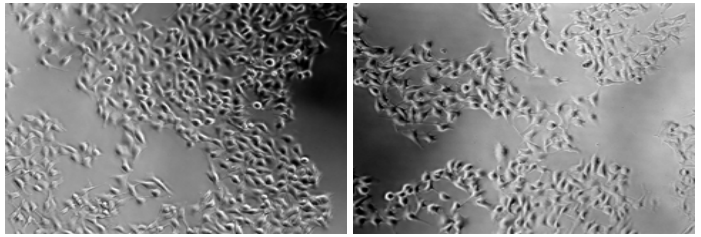
PG2(ET)

36 °C

heating



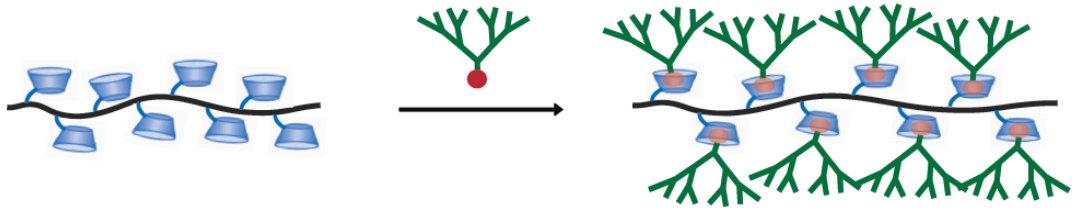
cooling

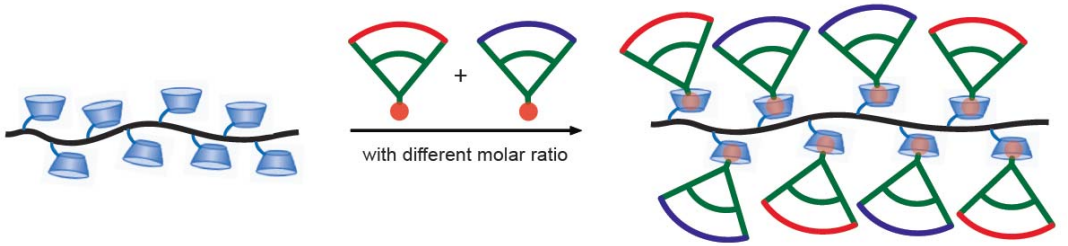


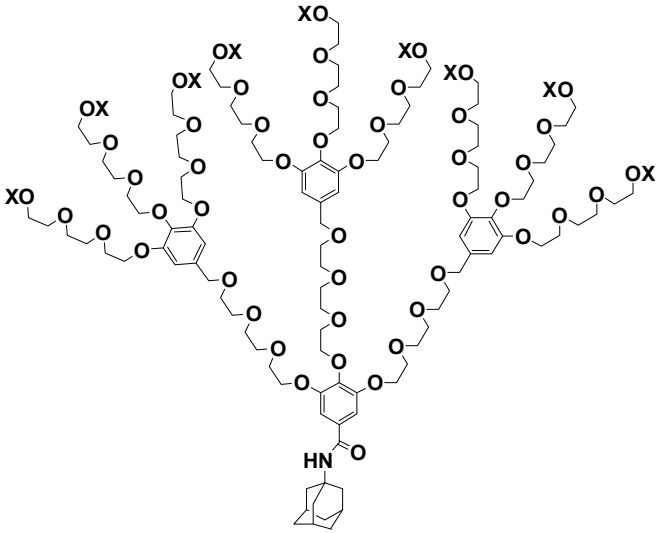
细胞毒性测试：无毒

Macromolecules **2008,** *41*, 43-49; *Macromolecules* **2008,** *41*, 3659-3667. *Chem. Commun.*, **2008**, 5523-5525; *Chem. Commun.*, **2008**, 5948-5950.*J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 4530-4534. *Macromolecules* **2009**, *42*, 7122–7128. *Angew. Chem. Int. Ed.* **2010**, *49*, 5683-5687.

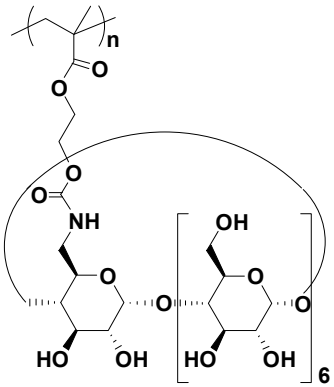
三、温度敏感智能树枝化聚合物（非共价型）



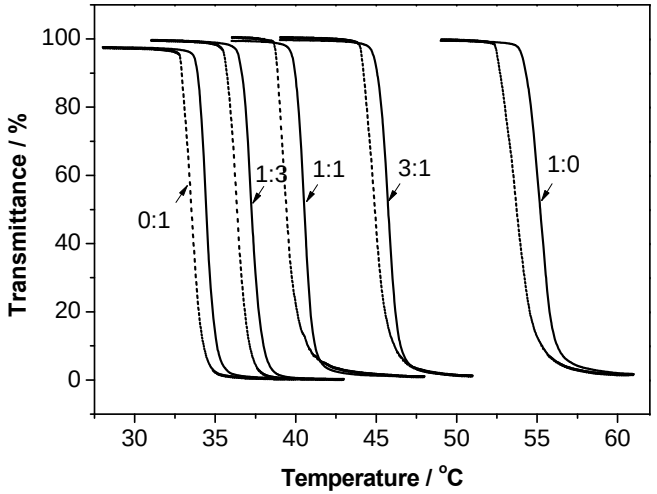




MeG2-Ada : X = Me
EtG2-Ada : X = Et

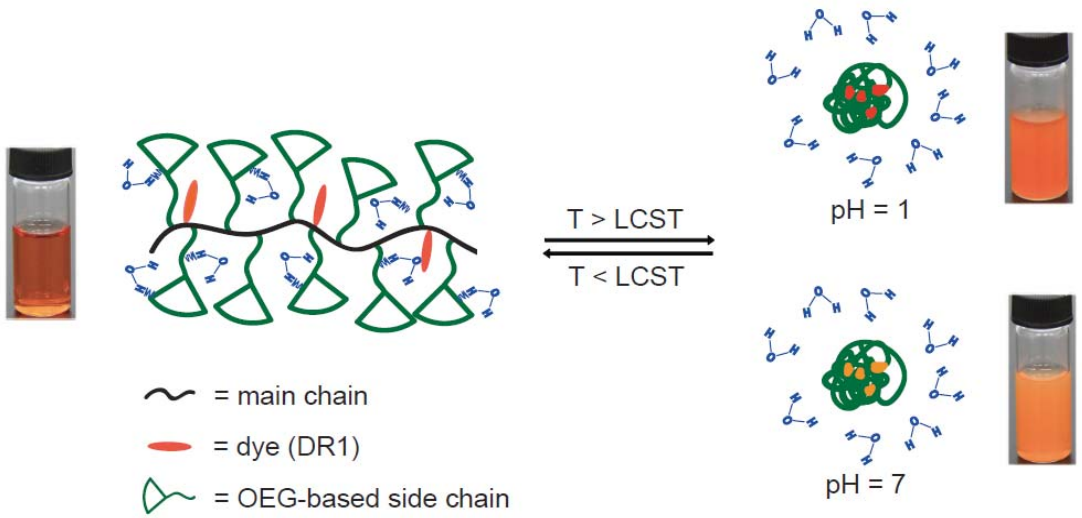


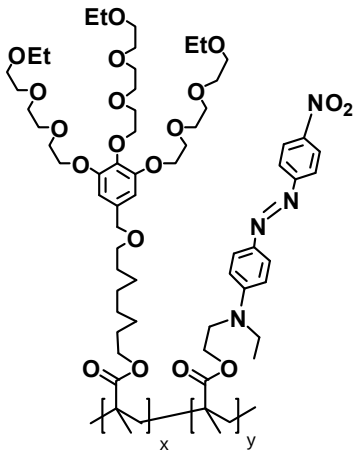
P-βCD



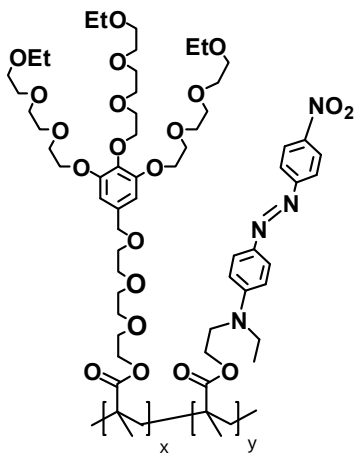
Chem. Asian J. **2011**, 6, 3260; *Soft Matter*, **2012**, 8, 6371.

四、温度敏感树枝化聚合物感应器





PG1(A)-*co*-DR1

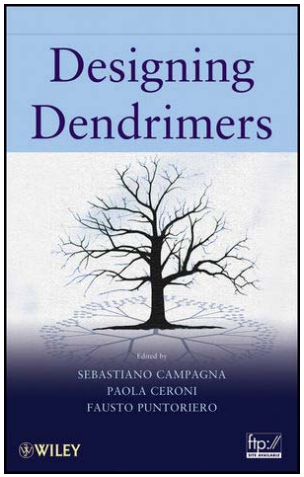


PG1(G)-*co*-DR1

Macromolecules **2011**, *44*, 8614–8621.

受邀撰写专著：

Afang Zhang, and A. Dieter Schlueter, Chapter 4 in **Designing Dendrimers** (ed. S. Campagna, P. Ceroni, and F. Puntoriero), pp 95-120. Wiley **2012**, Hoboken.



Wen Li, and Afang Zhang, **Stimuli-Responsive Dendronized Polymers.** *Encyclopedia of Polymer Science and Technology* **2012, accepted**

聚合物分子设计与合成实验室

网址：**www.polychem.shu.edu.cn**

Thanks for your attention !

Any Question?