Supramolecular Polymers

DOI: 10.1002/ange.201006999

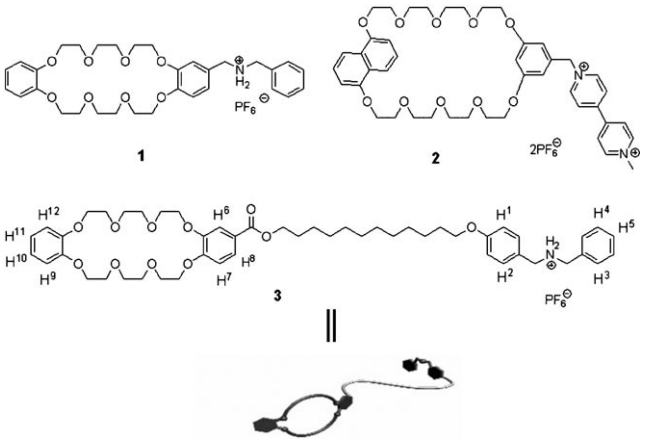
A Dual-Responsive Supramolecular Polymer Gel Formed by Crown Ether Based Molecular Recognition**

*Shengyi Dong, Yan Luo, Xuzhou Yan, Bo Zheng, Xia Ding, Yihua Yu, Zhi Ma, Qiaoling Zhao, and Feihe Huang**

Reversibility and responsiveness are ubiquitous in nature, whereby biological systems utilize stimuli-responsive aggregates to develop highly complicated and ordered materials. The realization of reversibility and responsiveness is of particular importance in the improvement of properties and the development of new materials. Supramolecular chemistry, through the use of noncovalent interactions, offers a platform to construct advanced and sophisticated materials through a bottom-up approach.[1] Supramolecular gels constructed from low molecular weight molecules by reversible noncovalent interactions is a kind of adaptive material that can be sensitive to the changes of pH value, temperature, solvent, chemical stimuli, and even the concentration of components.[2] Being responsive to multiple stimuli, these supramolecular gels are expected to be highly advantageous over traditional polymer gels and possess many unique properties that play a significant role in drug-delivery systems, molecular devices, or novel membranes.[3]

Various noncovalent interactions,[4] such as host–guest interactions, hydrogen bonds, and metal coordination, have been used to prepare supramolecular gels from low molecular weight molecules. Crown ethers, serving as the first generation of supramolecular hosts, have been widely used as building blocks to construct different functional assemblies with complementary guest molecules.[5] Although supramolecular alternating copolymers prepared from self-sorting organization of two heteroditopic monomers were reported by us,[1i] up to now, supramolecular polymer gels formed from small molecules by crown ether based molecular recognition have not been reported. Although Shinkai and co-workers have developed gelators comprised of crown ethers,[6] the driving forces for the gelation are largely attributed to the appended groups. It is still a big challenge to design and synthesize novel stimuli-responsive gels completely based on the host–guest interactions between crown ether and complementary guest moieties.

Stoddart's and Gibson's groups have found that A–B monomers **1** and **2** with the guest salt units directly attached to



crown ether moieties are favored to form [*c*2]daisy chains instead of linear supramolecular polymers.[7] To effectively construct the supramolecular polymer gels, attention should be paid to avoiding the formation of the cyclic oligomers. On the basis of a structural analysis of previously reported supramolecular polymer monomers, it was found that the long flexible alkyl linkers between the host and guest moieties not only favor the formation of linear supramolecular polymers, but also lead to a low critical suprapolymerization concentration (CPC).[1i,1,8] On the basis of such observations, we report herein the design and synthesis of a novel dual-responsive supramolecular polymer gel, which is constructed from a heteroditopic A–B monomer **3** utilizing the reversible host–guest interactions between dibenzo[24]crown-8 (DB24C8) and its complementary guest dibenzylammonium salt (DBA). It is well known that the dibenzo[24]crown-8 (DB24C8) moiety forms 1:1 threaded structure with the dibenzylammonium salt (DBA) moiety.[9] Our approach is that 1) the complexation of DB24C8 and DBA units can be responsive to two stimuli (pH value or temperature change) and 2) the flexible long alkyl chain favors the formation of

[*] S. Dong, Y. Luo, X. Yan, B. Zheng, Prof. Dr. F. Huang
Department of Chemistry, Zhejiang University
Hangzhou, Zhejiang 310027 (China)
Fax: (+86) 571-8795-3189
E-mail: fhuang@zju.edu.cn

X. Ding, Prof. Dr. Y. Yu
Shanghai Key Laboratory of Magnetic Resonance
Department of Physics, East China Normal University
Shanghai 200062 (China)

Assoc. Prof. Dr. Z. Ma, Q. Zhao
Shanghai Institute of Organic Chemistry
Chinese Academy of Science
Shanghai 200032 (China)

[**] This work was supported by the National Natural Science Foundation of China (20774086, 20834004), the Fundamental Research Funds for the Central Universities (2010QNA3008), the MOE Key Laboratory of Macromolecular Synthesis and Functionalization of Zhejiang University (2010MSF02), and the Zhejiang Provincial Natural Science Foundation of China (R4100009).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201006999.

linear supramolecular polymers. This monomer can form a supramolecular polymer gel in acetonitrile, and reversible sol–gel transitions can be realized by subsequent alteration of heating and cooling, or acidification and neutralization. The thermo- and pH-responsive gel–sol transitions were successfully employed in the controlled release of rhodamine B.

Linear supramolecular polymers in solution were first envisioned to be driven by host–guest interactions through the strong affinity between DB24C8 and DBA, which is the basis for the further formation of entangled self-assembled fibrillar networks. Defined as three-dimensional fiber networks, supramolecular polymer gels are derived from the self-organization of one-dimensional fibrils, which aggregate from those long supramolecular polymer chains; these supramolecular polymers assemble into bundles at first and subsequently form an entangled sample spanning network, which is capable of preventing the flow of bulk solvent. Through the entanglement of supramolecular fibrils, three-dimensional fiber networks are constructed and macroscopic organogels are finally formed by incorporating solvent molecules (Scheme 1).[2d,10]

^{1}H NMR studies provided important insights into the complexation behavior of monomer **3** in solution. The concentration-dependent ^{1}H NMR spectra of monomer **3** (Figure 1) were complicated by the slow-exchange complexation of the DB24C8 and DBA units on the proton NMR timescale. At low concentrations, peaks of cyclic oligomers and uncomplexed monomer were obvious, and no signals of linear species were observed (Figure 1 d–f), indicating a preference for the cyclic oligomers. As the initial monomer concentration was increased, the signals of $H^{1,lin}$, $H^{2,lin}$, and $H^{8,lin}$ related to linear supramolecular polymers became obvious. With the increase of initial monomer concentration, the cyclic species dominates at the beginning, and then its concentration decreases. By contrast, the concentration of linear species increases constantly, whereas the concentration of uncomplexed species increases, reaches a maximum at about 100 mM, and then decreases. The enhanced signals of the linear species as well as the gradual disappearance of cyclic species peaks, along with the broadening of all signals, confirmed the formation of high molecular weight aggregates driven by host–guest interactions between the DB24C8 host and DBA guest moieties.[8d] Those changes showed the competition between linear chain extension and cyclic oligomerization of monomer **3**.[1i,l,11]

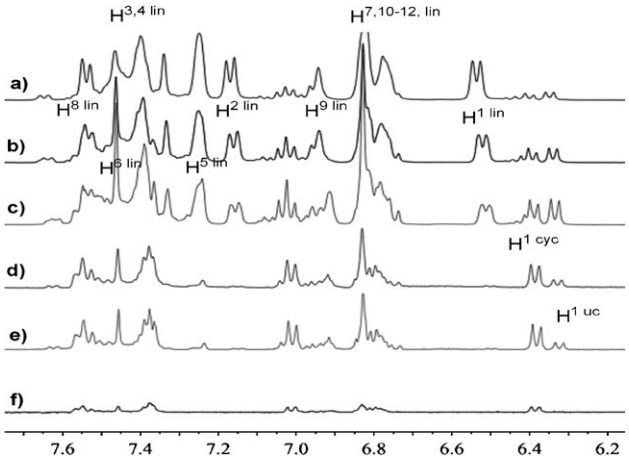
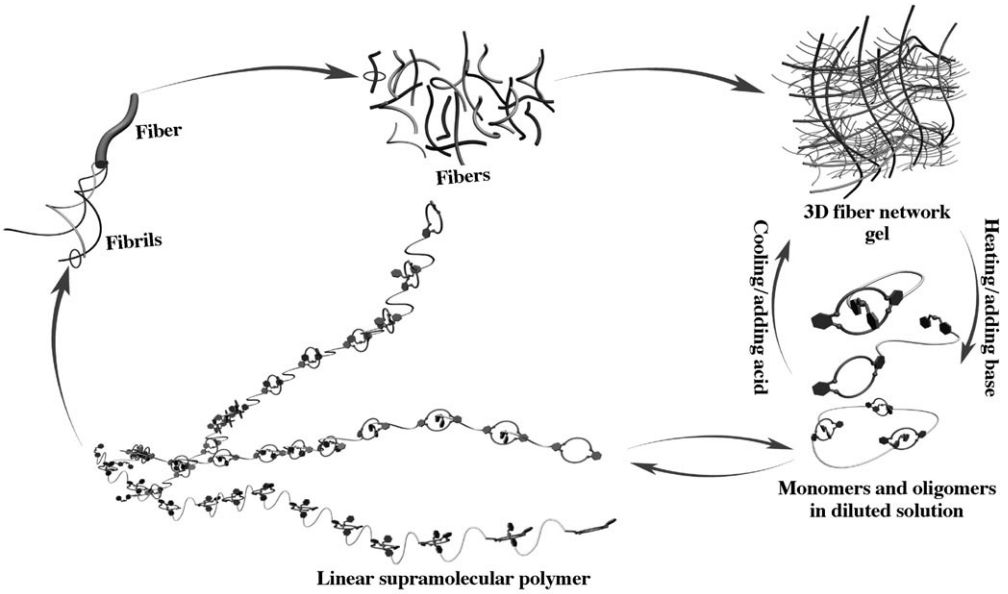


Figure 1. Partial ^{1}H NMR spectra of monomer **3** (400 MHz, [D_3]acetonitrile, 20 °C) at various concentrations: a) 400 mM; b) 200 mM; c) 100 mM; d) 10 mM; e) 5 mM; f) 1 mM. Peaks of linear polymer, cyclic oligomer, and uncomplexed monomer are designated by lin, cyc, and uc, respectively.[8d]

Two-dimensional diffusion-ordered NMR (DOSY) experiments (see Figure S6 in the Supporting Information) were also performed to investigate the self-assembly process of monomer **3** to form the supramolecular polymers. As the monomer concentration increased from 20 mM to 400 mM, the measured weighted average diffusion coefficient decreased considerably from $6.92(\pm0.35)\times10^{-10}\ m^2\,s^{-1}$ to $5.62(\pm0.28)\times10^{-11}\ m^2\,s^{-1}$, indicating the concentration dependence of supramolecular polymerization of monomer **3**. Based on the previous reports,[11] it is known that a high degree of polymerization value for the repeating unit is necessary to result in a 10-fold decrease in the diffusion coefficient. Hence, the current measurements clearly indicated the formation of an extended, high molecular weight polymer structure.

Viscosity is a direct index for the formation of polymers. Therefore, to further investigate the



Scheme 1. Formation of a supramolecular polymer gel through self-assembly of monomer **3**.

supramolecular aggregations in solution, a double logarithmic plot of specific viscosity versus concentration of monomer **3** in CH_3CN (see Figure S6 in the Supporting Information) was obtained. In the low concentration range, the curve had a slope of 1.02. As the concentration increased, the slope of the curve approached 2.32. The linear relationship (slope of 1.02) indicated the presence of noninteracting assemblies of a constant size, whereas an exponential relationship (slope > 2) is consistent with the presence of a supramolecular polymerization process, in which the size of the resulting polymer increased with concentration. The CPC for monomer **3** in CH_3CN was about 60 mM as evidenced by the clear change of slope occurring at this concentration, indicating a ring–chain transition from the formation of cyclic oligomers to highly ordered polymers; hence, the mobility of the polymeric chains is restricted.[1i,j,l,11]

Furthermore, rodlike fibers with a regular diameter of 8 μm were drawn from a high concentration solution and observed by scanning electron microscopy (SEM), providing direct evidence of the formation of supramolecular polymers with high molecular weight and a high degree of linear chain extension (see Figure 3a). Next, the gelation properties of the synthesized monomer **3** were investigated (Figure 2). The novel supramolecular polymer gel was prepared by dissolving monomer **3** in CH_3CN at 50 °C followed by cooling to room temperature. Upon increasing the concentration of monomer **3** from 10 mM to 35 mM, the solution became a mixture of solution and gel, and finally formed a gel at a phase-transition temperature of approximately 40 °C; the critical gel concentration was calculated to be 4.6 wt %.

It is generally known that the secondary ammonium salt unit can be deprotonated by adding base, thus destroying the host–guest recognition between DB24C8 and DBA and making the complex disassemble. Hence, the reversible gel–sol transition could be realized by changing the pH value. As shown in Figure 2, after the addition of several drops of triethylamine, the gel dissociated into a transparent solution within a short time. Re-formation of the gel from the sol state was achieved by adding a little excess trifluoroacetic acid. This process was also demonstrated by ^{1}H NMR experiments (see the Supporting Information) and SEM experiments (see the Supporting Information). The addition of 20 μL of triethylamine to a solution of monomer **3** in [D_3]acetonitrile (50 mM, 0.5 mL) caused remarkable changes of the proton chemical shifts (Figure S7a,b). Almost all complexed signals disappeared, sharp signals of uncomplexed protons H^8, H^6, and H^1 appeared, and the signals of protons H^3 and H^4 exhibited upfield shifts. All these observations suggested that the host–guest interactions were destroyed completely and the complexation between DB24C8 and DBA was totally quenched. After 14.0 μL of trifluoroacetic acid was added, the host–guest complexation was recovered and the complicated complexed signals were observed again (Figure S7c).[6b,12] In addition, this reversible decomplexation–complexation transition could be repeated (Figure S7d,e).

Also, the host–guest interaction between the DB24C8 and DBA units could be reduced by heating, as shown by ^{1}H NMR experiments. The variable-temperature ^{1}H NMR spectra of monomer **3** in [D_3]acetonitrile (see Figure S8 in the Supporting Information) provided direct evidence for the assembly process from gel to sol state. At a relatively low temperature (268 K), the ^{1}H NMR signals of monomer **3** almost disappeared, suggesting strong intermolecular aggregation. By gradually raising the temperature, the original weak and broad signals became well-dispersed and can be easily identified. These results showed a remarkable temperature-dependent behavior and suggested that the formation of the gel was weakened at elevated temperatures and eventually disrupted,[13] which was consistent with the above gelation test (Figure 2).

Thus, by adjusting the pH and temperature of the solution, the gelation process can be manipulated to control a range of gel properties, such as the gelation time, gel transparency, gel morphology, and the gel–sol transition.

Xerogels, prepared by freeze-drying the gels of monomer **3** in CH_3CN, were examined by SEM, revealing an extended and interconnected fibrous gel network. The SEM images showed long fibers and well-developed three-dimensional network structures of fibers with diameters of 1–2 μm and lengths of several hundred micrometers (Figure 3b). The formation of fibers is a typical characteristic for the entanglement of linearly connected macrosized aggregates. These self-assembled fibers physically cross-linked together to form a fibrous network as the matrix of the gel.[10a] This extended network further interweaved and tangled with fibers to form a very dense gel network

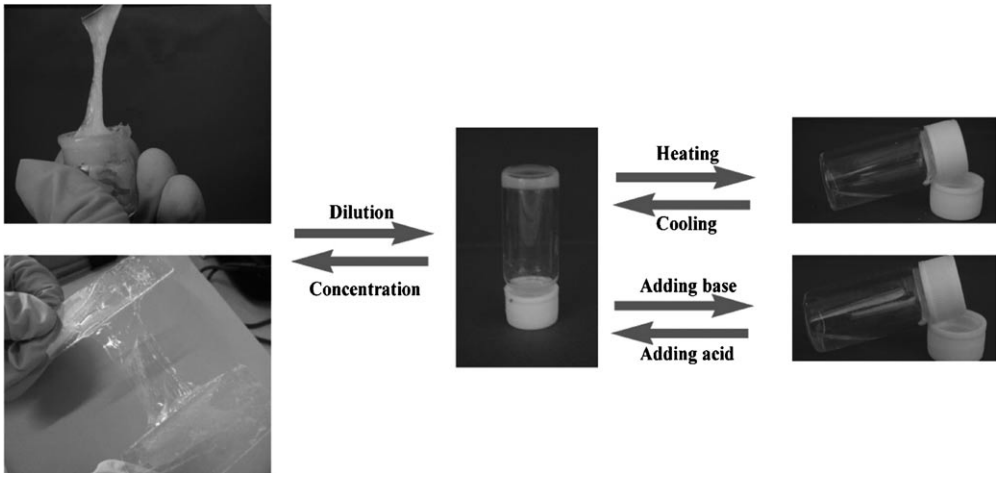


Figure 2. Supramolecular gel, its gel–sol transitions triggered by stimuli (temperature and pH), and supramolecular aggregates (glue-like viscous liquids and transparent films).

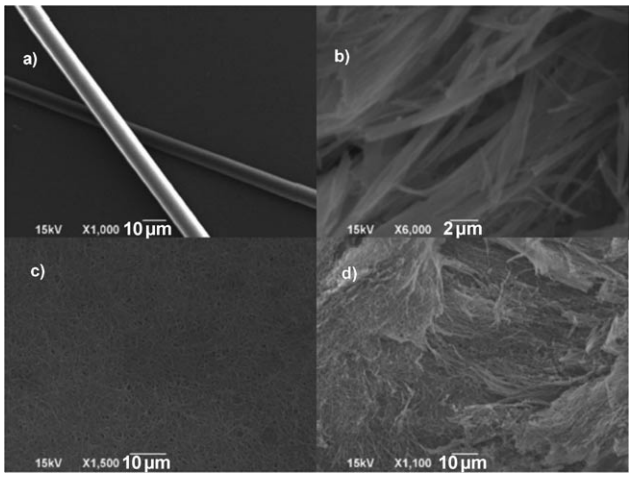


Figure 3. SEM images of aggregates: a) rod-like fibers; b–d) structure of the three-dimensional network.

(Figure 3c,d). These xerogels can be destroyed by adding triethylamine (see the Supporting Information).

Rhodamine B was used as a model compound to investigate the potential of the supramolecular polymer gel as a thermo- and pH-controlled release system.[14] Prior to heating or addition of triethylamine, the layer of water was colorless at room temperature, which indicated that rhodamine B remained entrapped inside the gel matrix and was not released to the water. After addition of a small excess amount of triethylamine, the gel was gradually disrupted and the color of the layer of water turned from pink to dark red, indicating that rhodamine B was released from the gel. The release of rhodamine B could also be induced by heating (see Figure S9 in the Supporting Information). From 30 °C to 50 °C, the color of the layer of water turned from pale red to red. At 50 °C, the gel was destroyed and the rhodamine B molecules were completely released. All these observations were consistent with the UV/Vis absorption measurements (see Figure S9 in the Supporting Information).

It is worth noting that with increasing concentration of monomer **3** in CH_3CN at room temperature, dramatic changes in material properties were observed (Figure 2). Glue-like viscous liquids were formed by dissolving monomer **3** in CH_3CN at the concentration of about 1.0 M, whereas flexible, transparent, and amorphous films were cast from more concentrated solutions (> 1.5 M). All of these morphologies were typical characteristics for entanglement of linearly connected macro-sized supramolecular aggregates. Such properties showed the reversibility of the host–guest interactions and the chain extension.[9,15]

In conclusion, we prepared a dual-responsive supramolecular polymer gel driven by crown ether based molecular recognition. The system has pH- and thermo-responsive abilities. Long flexible alkyl chains were found to contribute to the formation of linear supramolecular polymers, which play an important role as physical junctions in supramolecular gels. The supramolecular polymer gel showed reversible gel–sol phase transitions by heating and cooling, or by adding base and acid. The thermo- and pH-responsive gel–sol transition was successfully employed for the controlled release of rhodamine B. We demonstrated the reversibility, versatility, and multiresponsiveness of supramolecular polymer gel constructed by an asymmetric complementary A–B monomer. The work presented herein also demonstrated that the complex of DB24C8 and DBA can be used as a building block to construct multiple supramolecular aggregates from supramolecular polymer gels, viscous liquids, fibers to transparent films under different conditions. This dual-responsive supramolecular polymer gel is promising as a unique advanced material with applications in biomedical fields, personal-care products, and drug-delivery systems.

Received: November 8, 2010
Published online: January 12, 2011

Keywords: crown compounds · host–guest systems · molecular recognition · sol–gel processes · supramolecular chemistry

[1] a) C. Fouquey, J. M. Lehn, A. M. Levelut, *Adv. Mater.* **1990**, *2*, 254–257; b) R. P. Sijbesma, F. H. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, *Science* **1997**, *278*, 1601–1604; c) B. J. B. Folmer, R. P. Sijbesma, R. M. Verseegen, J. A. J. van der Rijt, E. W. Meijer, *Adv. Mater.* **2000**, *12*, 874–878; d) L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071–4098; e) W. Binder, R. Zirbs, *Adv. Polym. Sci.* **2007**, *207*, 1–78; f) J. Gao, Y. He, H. Xu, B. Song, X. Zhang, Z. Wang, X. Wang, *Chem. Mater.* **2007**, *19*, 14–17; g) B. Song, H. Wei, Z. Wang, X. Zhang, M. Smet, W. Dehaen, *Adv. Mater.* **2007**, *19*, 416–420; h) T. F. A. De Greef, E. W. Meijer, *Nature* **2008**, *453*, 171–173; i) F. Wang, C. Y. Han, C. L. He, Q. Z. Zhou, J. Q. Zhang, C. Wang, N. Ling, F. H. Huang, *J. Am. Chem. Soc.* **2008**, *130*, 11254–11255; j) T. F. A. De Greef, M. M. J. Smulders, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2009**, *109*, 5687–5754; k) A. Harada, Y. Takashima, H. Yamaguchi, *Chem. Soc. Rev.* **2009**, *38*, 875–882; l) F. Wang, J. Q. Zhang, X. Ding, S. Y. Dong, M. Liu, B. Zheng, S. J. Li, L. Wu, Y. H. Yu, H. W. Gibson, F. H. Huang, *Angew. Chem.* **2010**, *122*, 1108–1112; *Angew. Chem. Int. Ed.* **2010**, *49*, 1090–1094; m) Y. Liu, Y. Yu, J. Gao, Z. Wang, X, Zhang, *Angew. Chem.* **2010**, *122*, 6726–6729; *Angew. Chem. Int. Ed.* **2010**, *49*, 6576–6579.

[2] a) K. M. Huh, Y. W. Cho, H. Chung, I. C. Kwon, S. Y. Jeong, T, Ooya, W. K. Lee, S, Sasaki, N. Yui, *Macromol. Biosci.* **2004**, *4*, 92–99; b) H. S. Choi , K. Yamamoto , T. Ooya, N. Yui, *ChemPhysChem* **2005**, *6*, 1081–1082; c) I. Hwang, W. S. Jeon, H. J. Kim, D. W. Kim, H. Kim, N. Selvapalam, N. Fujita, S. Shinkai, K. Kim, *Angew. Chem.* **2007**, *119*, 214–217; *Angew. Chem. Int. Ed.* **2007**, *46*, 210–213; d) H. Komatsu, S. Matsumoto, S. I. Tamaru, K. Kaneko, M. Ikeda, I. Hamachi, *J. Am. Chem. Soc.* **2009**, *131*, 5580–5585; e) X. J. Liao, G. S. Chen, X. X. Liu, W. X. Chen, F. E. Chen, M. Jiang, *Angew. Chem.* **2010**, *122*, 4511–4515; *Angew. Chem. Int. Ed.* **2010**, *49*, 4409–4413.

[3] a) S. Sivakova, D. A. Bohnsack, M. E. Mackay, P. Suwanmala, S. J. Rowan, *J. Am. Chem. Soc.* **2005**, *127*, 18202–18211; b) M. Suzuki, C. Setoguchi, H. Shirai, K. Hanabusa, *Chem. Eur. J.* **2007**, *13*, 8193–8200; c) Y. Yang, T. Chen, J. F. Xiang, H. J. Yan, C. F. Chen, L. J. Wan, *Chem. Eur. J.* **2008**, *14*, 5742–5746; d) D. K. Smith, *Chem. Soc. Rev.* **2009**, *38*, 684–694.

[4] a) Y. Q. Zhao, B. J. Beck, S. J. Rowan, A. M. Jamieson, *Macromolecules* **2004**, *37*, 3529–3531; b) W. G. Weng, J. B. Beck, A. M. Jamieson, S. J. Rowan, *J. Am. Chem. Soc.* **2006**, *128*, 11663–11672; c) W. Deng, H. Yamaguchi, Y. Takashima, A. Harada,

Angew. Chem. **2007**, *119*, 5236 – 5239; *Angew. Chem. Int. Ed.* **2007**, *46*, 5144 – 5147; d) B. Jing, X. Chen, X. D. Wang, Y. R. Zhao, H. Y. Qiu, *ChemPhysChem* **2008**, *9*, 249 – 252; e) W. Deng, H. Yamaguchi, Y. Takashima, A. Harada, *Chem. Asian J.* **2008**, *3*, 687 – 695; f) W. G. Weng, Z. Li, A. M. Jamieson, S. J. Rowan, *Macromolecules* **2009**, *42*, 236 – 246.

[5] a) *Molecular Catenanes, Rotaxanes and Knots* (Eds.: J.-P. Sauvage, C. Dietrich-Buchecker), Wiley-VCH, Weinheim, **1999**; b) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484 – 3530; *Angew. Chem. Int. Ed.* **2000**, *39*, 3348 – 3391; c) C. A. Schalley, K. Beizai, F. Vögtle, *Acc. Chem. Res.* **2001**, *34*, 465 – 476; d) J. P. Collin, C. D. Buchecker, P. Gavina, M. C. J. Molero, J. P. Sauvage, *Acc. Chem. Res.* **2001**, *34*, 477 – 487; e) T. Takata, N. Kihara, Y. Furusho, *Adv. Polym. Sci.* **2004**, *171*, 1 – 75; f) T. Oku, Y. Furusho, T. Takata, *Angew. Chem.* **2004**, *116*, 984 – 987; *Angew. Chem. Int. Ed.* **2004**, *43*, 966 – 969; g) S. J. Loeb, *Chem. Commun.* **2005**, 1511 – 1518; h) J.-P. Collin, V. Heitz, J.-P. Sauvage, *Top. Curr. Chem.* **2005**, *262*, 26 – 62; i) F. H. Huang, H. W. Gibson, *Prog. Polym. Sci.* **2005**, *30*, 982 – 1018; j) W. Ong, J. Grindstaff, D. Sobransingh, R. Toba, J. M. Quintela, C. Peinador, A. E. Kaifer, *J. Am. Chem. Soc.* **2005**, *127*, 3353 – 3361; k) G. Wenz, B. H. Han, A. Mueller, *Chem. Rev.* **2006**, *106*, 782 – 817; l) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem.* **2007**, *119*, 72 – 196; *Angew. Chem. Int. Ed.* **2007**, *46*, 72 – 191; m) J. J. Gassensmith, J. M. Baumes, B. D. Smith, *Chem. Commun.* **2009**, 6329 – 6338; n) Z. B. Niu, H. W. Gibson, *Chem. Rev.* **2009**, *109*, 6024 – 6046.

[6] a) J. H. Jung, H. Kobayashi, M. Masuda, T. Shimizu, S. Shinkai, *J. Am. Chem. Soc.* **2001**, *123*, 8785 – 8789; b) S. I. Kawano, N. Fujita, S. Shinkai, *Chem. Commun.* **2003**, 1352 – 1353; c) J. H. Jung, S. J. Lee, J. A. Rim, H. Lee, T. S. Bae, S. S. Lee, S. Shinkai, *Chem. Mater.* **2005**, *17*, 459 – 462.

[7] a) P. R. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1344 – 1347; *Angew. Chem. Int. Ed.* **1998**, *37*, 1294 – 1297; b) P. R. Ashton, I. W. Parsons, F. M. Raymo, J. F. Stoddart, A. J. P. White, D. J. Williams, R. Wolf, *Angew. Chem.* **1998**, *110*, 2016 – 2019; *Angew. Chem. Int. Ed.* **1998**, *37*, 1913 – 1916; c) H. W. Gibson, N. Yamaguchi, Z. B. Niu, J. W. Jones, C. Slebodnick, A. L. Rheingold, L. N. Zakharov, *J. Polym. Sci. Part A* **2010**, *48*, 975 – 985.

[8] a) N. Yamaguchi, D. S. Nagvekar, H. W. Gibson, *Angew. Chem.* **1998**, *110*, 2518 – 2520; *Angew. Chem. Int. Ed.* **1998**, *37*, 2361 – 2364; b) N. Yamaguchi, H. W. Gibson, *Chem. Commun.* **1999**, 789 – 790; c) N. Yamaguchi, H. W. Gibson, *Angew. Chem.* **1999**, *111*, 195 – 199; *Angew. Chem. Int. Ed.* **1999**, *38*, 143 – 147; d) H. W. Gibson, N. Yamaguchi, J. W. Jones, *J. Am. Chem. Soc.* **2003**, *125*, 3522 – 3533.

[9] P. R. Ashton, E. J. T. Chrystal, P. Glink, T. S. Menzer, C. Schiavo, N. Spencer, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 709 – 728.

[10] a) N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821 – 836; b) J. D. Fox, S. J. Rowan, *Macromolecules* **2009**, *42*, 6823 – 6835.

[11] F. Wang, B. Zheng, K. L. Zhu, Q. Z. Zhou, C. X. Zhai, S. J. Li, N. Li, F. H. Huang, *Chem. Commun.* **2009**, 4375 – 4377.

[12] K. C.-F. Leung, P. M. Mendes, S. N. Magonov, B. H. Northrop, S. Kim. K. Patel, A. H. Flood, H.-R. Tseng, J. F. Stoddart, *J. Am. Chem. Soc.* **2006**, *128*, 10707 – 10715.

[13] R. K. Cao, J. J. Zhou, W. Wang, W. Feng, X. H. Li, P. H. Zhang, P. C. Deng, L. H. Yuan, B. Gong, *Org. Lett.* **2010**, *12*, 2958 – 2961.

[14] K. Peng, I. Tomatsu, A. Kros, *Chem. Commun.* **2010**, *46*, 4094 – 4096.

[15] J. B. Beck, J. M. Ineman, S. J. Rowan, *Macromolecules* **2005**, *38*, 5060 – 5068.

