Poly[2]-catenanes containing alternating topological and covalent bonds

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A poly[2]-catenane containing interlocking 45-membered rings is synthesized; the polymer backbone includes alternating topological links and covalent bonds.

Macromolecular systems containing interlocking rings (catenanes) and rotaxane-like elements are of special interest.[1,2] In particular, introduction of topological bonds in the main chain of the polymer has been considered as a synthetic challenge for decades. In addition, large catenanes contain elements of mobility which make such macromolecules particularly attractive from the viewpoint of their potential rheological and mechanical properties. Poly[2]-catenanes represent the prototypical example of such architectures.

We now report that a difunctionalized catenane, made of large and rigid macrocycles (45-membered rings, incorporating aromatic units), has been synthesized and copolymerized with a rigid spacer, to afford the desired macromolecular architecture. The polymer structure (**1**) thus obtained contains alternating topological links (interlocking rings) and covalent bonds.

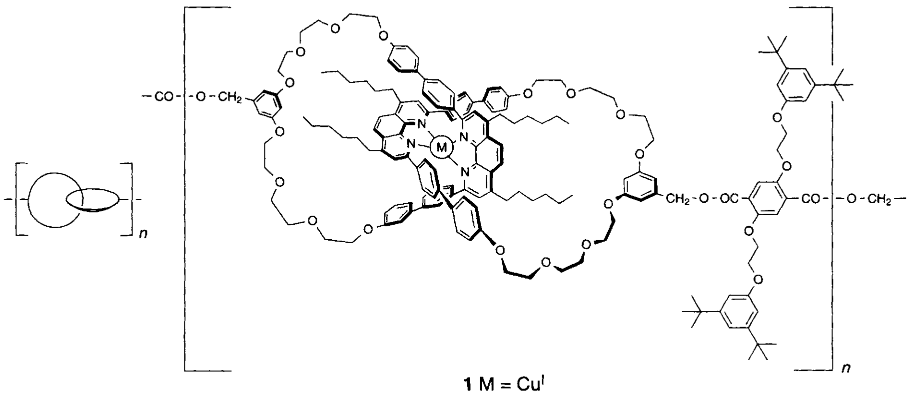
The monomer precursors were prepared following a three-dimensional templated strategy developed in the Strasbourg group for several years.[3] Large rings were used in order to ensure pronounced mobility of the demetallated system (**2**: M absent) and solubilizing groups were introduced so as to counterbalance the expected effect of 1,10-phenanthroline and biphenyl nuclei.

The intermediate compounds made and the final monomers [copper(I) catenate **8** or catenand **10**] are depicted in Fig. 1.

Compound **3** was obtained from 5-carbomethoxyresorcinol and the monochloro derivative of triethyleneglycol (NaH in dmf), followed by mesylate formation and treatment with NaI. Compound **4** was prepared by reacting 4-lithio-4′-triisopropylsilyloxybiphenyl with 4,7-di-*n*-hexyl-1,10-phenanthroline, followed by hydrolysis and MnO_2 reoxidation, similarly to a literature procedure.[4] The silyl groups were cleaved off using NBu_4F. The macrocyclic compound **6** was synthesized by reacting **3** and **5** under high-dilution conditions in the presence of Cs_2CO_3 (60 °C, dmf, 53% yield). Compound **5** was threaded through **6** using $[Cu(MeCN)_4]PF_6$ as template and the pseudorotaxane intermediate formed was cyclized (55% yield) using **3** and Cs_2CO_3 in a procedure similar to the preparation of **6**. The copper(I) catenate **7** obtained bears two ester functions which were reduced by Hdibal to afford **8** (64% yield from **7**). Demetallation of **7** (KCN in CH_2Cl_2–MeCN–H_2O) led to **9** in 68% yield. The corresponding dibenzylic alcohol **10** was obtained in 73% yield, using the same conditions as for the reduction of **7**. Typically, **8** and **10** were prepared at the 0.2 gram scale. Their analytical data (^1H and ^{13}C NMR and FAB MS) were in accordance with their structure.

The polycondensation reactions were carried out between diacid **11** and the diols **8** or **10**, affording poly[2]-catenate **1** or poly[2]-catenand **2**, respectively. A direct polyesterification method was applied,[5] in dichloromethane using *N,N*′-diisopropylcarbodiimide as a reagent and 4-(*N,N*′-dimethylamino)pyridine toluene-*p*-sulfonic acid 1 : 1 complex as catalysts. Polymerisation was carried out for 3 d at −10 °C, then 2 d at 0 °C and finally 1 d at room temperature. The polymers were soluble in chlorinated solvents and thf, and purified by precipitation in a non-solvent (diethyl ether for the poly[2]-catenate **1** and methanol for the poly[2]-catenand **2**). Gel permeation chromatography (GPC) in chloroform (calibration with polystyrene standards), indicated that high-molecular-mass poly[2]-catenate and poly[2]-catenand were obtained (Fig. 2).

Number-average molecular mass (M_n) and mass-average molecular mass (M_w) values were: 6.0×10^5 and 4.2×10^6 for poly[2]-catenate; 5.5×10^4 and 1.8×10^6 for poly[2]-catenand. ^1H and ^{13}C NMR spectroscopy confirmed the presence of linear high-molecular mass polymers. In the ^1H NMR spectra, all peaks were broadened compared to the corresponding monomers, as expected for polymers. Typical resonances of the spacer and of the interlocked macrocycles were present. No



1 M = Cu^I
2 M absent

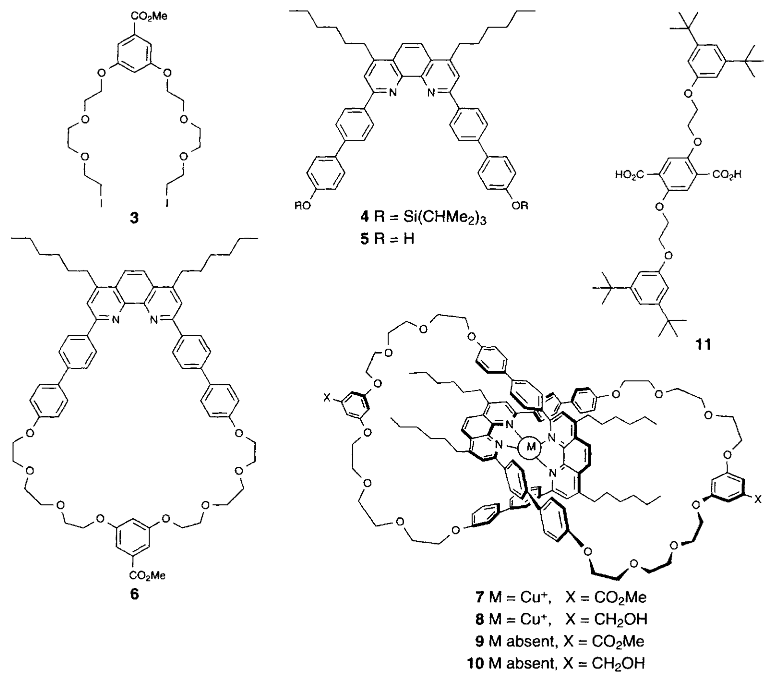


Fig. 1 Chemical formulae of the molecules prepared in the present work

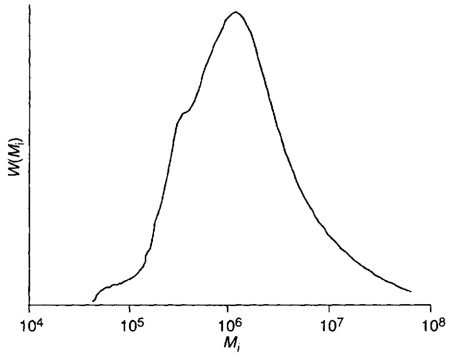


Fig. 2 Typical GPC curve for poly[2]-catenate **1** in $CHCl_3$

evidence of ring opening and dethreading during polymerisation was observed. New resonances appeared, namely benzyl ester protons at δ 5.25 and 5.17 for the poly[2]-catenate and for the poly[2]-catenand, respectively. ^1H NMR end-group analysis revealed that no more benzylic alcohol protons (CH_2OH) which appeared at δ 4.43 and 4.65 for the catenand and the catenate, respectively, were present in the corresponding polymer spectra. Accordingly, ^{13}C NMR spectra indicated that the characteristic resonance of the acid functions of the spacer at δ 163.8 was shifted to 165.0 and 164.9 (ester groups) for **1** and **2** respectively. The absence of end groups is in agreement with the high molecular masses observed by GPC. Thermogravimetric analysis showed that poly[2]-catenate **1** is stable up to 210 °C, whereas poly[2]-catenand **2** exhibited an even higher thermal stability of up to 300 °C. Second-order transitions, which are attributed to glass transitions, were observed by differential scanning calorimetry at *ca.* 60 and 75 °C for **1** and **2** respectively.

The production of poly[2]-catenanes on a larger scale, their full characterization by matrix assisted laser desorption mass spectrometry and membrane osmometry, as well as the study of their unusual mechanical and rheological properties are underway.

References

1 H. W. Gibson, M. C. Bheda and P. T. Engen, *Prog. Polym. Sci.*, 1994, **19**, 843; H. W. Gibson, S. Liu, P. Lecavalier, C. Wu and Y. X. Shen, *J. Am. Chem. Soc.*, 1995, **117**, 852; Y. S. Lipatov, T. E. Lipatova and L. F. Kosyanchuk, *Adv. Polym. Sci.*, 1989, **88**, 49; T. J. Fyvie, H. L. Frisch, J. A. Semlyen, S. J. Clarson and J. E. Mark, *J. Polym. Sci. A*, 1987, **25**, 2503; Topology in Molecular Chemistry, *New J. Chem.*, 1993, **17** (No. 10, 11), special issue and references cited therein; Y. Geerts, D. Muscat and K. Müllen, *Macromol. Chem. Phys.*, 1995, **196**, 3425; G. Bidan, B. Divisia-Blohorn, M. Lapkowski, J.-M. Kern and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1992, **114**, 5986.

2 For a recent and general discussion on catenanes, rotaxanes and knots, see: D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725.

3 C. O. Dietrich-Buchecker, J.-P. Sauvage and J.-P. Kintzinger, *Tetrahedron Lett.*, 1983, **24**, 5095; J.-P. Sauvage, *Acc. Chem. Res.*, 1990, **23**, 319.

4 C. O. Dietrich-Buchecker and J.-P. Sauvage, *Tetrahedron*, 1990, **46**, 503.

5 J. S. Moore and S. I. Stupp, *Macromolecules*, 1990, **23**, 65.

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