J|A|C|S
COMMUNICATIONS

Published on Web 07/27/2002

Hyperbranched Molecular Nanocapsules: Comparison of the Hyperbranched Architecture with the Perfect Linear Analogue

Salah-Eddine Stiriba, Holger Kautz, and Holger Frey*

Institut für Makromolekulare Chemie and Freiburger Materialforschungzentrum FMF, Albert-Ludwigs-Universität, Stefan-Meier-Strasse 21/31, D-79104 Freiburg, Germany

Received May 8, 2002

Hyperbranched polymers prepared in one step from AB_m-type monomers have captured considerable attention over the past few years.[1] Hyperbranched polymers show a distribution of functional end groups throughout their globular structure, in contrast to the perfectly branched dendrimers.[1b]

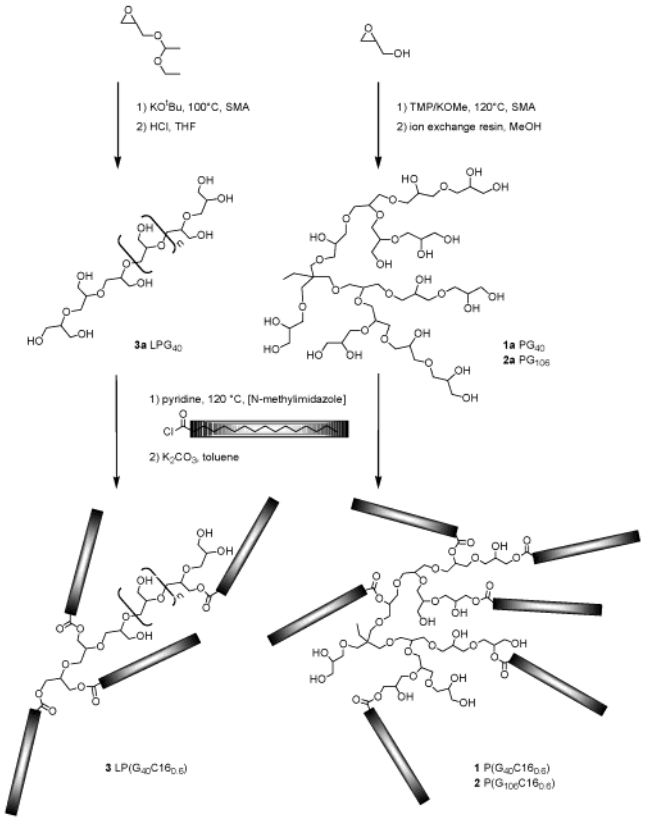
Currently, there is little data on the physical properties of dendrimers or hyperbranched polymers vis-à-vis their respective linear analogues. An elegant recent study has been reported for polybenzyl ethers.[2] The ability to encapsulate guest molecules or catalytically active moieties represents an important structural peculiarity of dendrimers.[3−5] Encapsulation can be achieved by core−shell amphiphilicity, as pioneered by Newkome et al.[5a] with the concept of the "unimolecular micelle" as well as via steric densification of the periphery, introduced by Meijer et al. as a "dendritic box".[5b]

However, in recent work, our group demonstrated that hyperbranched polyglycerols[6] with amphiphilic core−shell structure ("molecular nanocapsules"), conveniently prepared in two synthetic steps, exhibit unimolecular reverse micelle properties, i.e., encapsulation and phase transfer of ionic guest molecules[7] in analogy to amphiphilic dendrimers. The synthesis of such molecular nanocapsules makes use of the ring opening multibranching polymerization of glycidol under slow monomer addition (SMA), resulting in flexible aliphatic polyether−polyols with narrow polydispersities ($1.2 < M_w/M_n < 1.5$).[6] Subsequent, partial esterification of these hyperbranched polyglycerols using fatty acid chlorides afforded the amphiphilic polyglycerols **1** and **2** that quantitatively extract various dyes from the aqueous phase into apolar media,[7] stabilize nanosize Pd colloids,[8a] and are able to extract catalytically active polar pincer Pt(II) complexes.[8b]

The intriguing phase transfer properties of hyperbranched polyglycerol nanocapsules have been explained by their hydrophobic shell/hydrophilic core structure.[7] Since numerous linear polymer amphiphiles and polysoaps are known,[9] the key question is whether the hyperbranched topology is an actual prerequisite for the solvation behavior and if an analogous linear macromolecule with hydrophilic and hydrophobic moieties can encapsulate guests in a similar manner.

Here we report on a comparative study of the linear esterified polyglycerol **3** with the partially esterified hyperbranched polyglycerols **1** and **2** (Figure 1). Two polyglycerol samples **1a** and **2a** based on hyperbranched polyglycerols with molecular weights of 3000 and 8000 ($M_w/M_n = 1.3$), respectively, were partially esterified using palmitoyl chloride (C16). Esterification of 60% of the hydroxyl groups resulted in the polyglycerol samples $P(G_{40}C16_{0.6})$ **1** and $P(G_{106}C16_{0.6})$ **2** (Scheme 1).[10]

Scheme 1



For the preparation of the linear analogue of the hyperbranched polyglycerols, a modification of a reported synthetic protocol[11] was applied, based on the slow addition of ethoxy ethyl glycidyl ether to KO^{t}Bu. After cleavage of the acetal groups, linear polyglycerol **3a** of narrow polydispersity ($M_w/M_n = 1.3$) with a molecular weight of 3000 g/mol (VPO) was obtained.

Esterification of 60% of the hydroxyl groups of **3a** with palmitoyl chloride yielded the esterified linear polyglycerol $LP(G_{40}C16_{0.6})$ (**3**), using the same esterification method as for **1** and **2** (Scheme 1). Characterization of linear and hyperbranched polyglycerols and the esterified derivatives was achieved by ^1H and ^{13}C NMR, SEC, and VPO (cf. Supporting Information).

With the linear esterified polyglycerol **3** and the analogous hyperbranched polyglycerol samples **1** and **2** in hand, a comparison of the encapsulation and phase transfer properties of **1** and **2** with **3** concerning the entrapment of sulfonated, water-soluble dye probes (e.g., Congo Red) was performed. The dye was dissolved in water and the aqueous phase extracted with an apolar solvent containing the amphiphilic polyglycerols. The amount of dye transferred into

* To whom correspondence should be addressed. E-mail: holger.frey@fmf.uni-freiburg.de.

10.1021/ja026835m CCC: $22.00

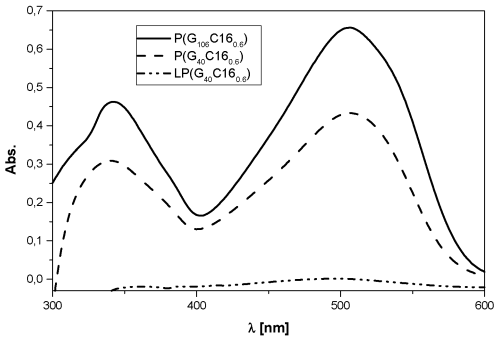


Figure 1. UV−vis spectra of **1**, **2**, and **3** (linear) after transfer of Congo Red dye into chloroform solution ([Congo Red]/[polymer] = 2).

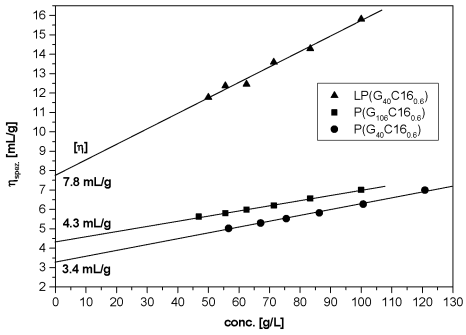


Figure 2. Specific viscosity vs concentration of **1**−**3** in toluene.

the organic phase by the polyglycerol-amphiphiles was monitored by UV−vis spectroscopy at different dye concentrations. The results (Figure 1) demonstrate unambiguously the crucial role of the hyperbranched topology. Both hyperbranched polymers **1** and **2** exhibit the expected phase transfer,[7] with saturation concentrations of 0.9 and 1.3 dye molecules per amphiphilic polymer molecule, respectively. In contrast, the analogous linear esterified polyglycerol showed no phase transfer at all for Congo Red and several other water-soluble dyes. Thus, molecular encapsulation is clearly a peculiarity of the hyperbranched topology and is related to the core−shell-type amphiphilicity of these polymers.

To gain insight into the nature of this strikingly different encapsulation behavior, specific and intrinsic viscosities of **1** to **3** in various apolar solvents were measured. Determination of the concentration-dependent specific viscosity is an important method to investigate the solution conformation of macromolecules. As a typical example, the behavior in toluene solution is shown in Figure 2. On one hand, the specific viscosity η_{sp} of the hyperbranched samples **1** and **2** is considerably lower than η_{sp} of the linear sample **3** at all concentrations. For instance, η_{sp} values of 10 wt % toluene solutions of **1**, **2**, and **3** were 6.2, 7.0, and 15.8 mL/g, respectively. In addition, the slope of the η_{sp} vs concentration plot is considerably lower for both hyperbranched nanocapsules **1** and **2** in comparison to that of **3** despite the three times higher molar mass of **2** compared to **3**. Extrapolation of η_{sp} to $c = 0$ yields intrinsic viscosities $[\eta] =$ 3.4 (**1**), 4.3 (**2**), and 7.8 mL/g (**3**). These viscosity data point to an extremely compact (dense) structure for the hyperbranched nanocapsules **1** and **2** in apolar media, in contrast to the linear sample **3** that possesses an open solution conformation.[12] This observation is explained by the preferential interaction of the polar core hydroxyl groups with themselves and the unfavorable interaction with nonpolar media.

The results show that a conformational collapse in solution leading to hard-sphere behavior is *only* possible in the case of the hyperbranched core−shell architecture.

Thermal properties of the samples **1**−**3** have also been studied, using differential scanning calorimetry (DSC). The solid-state properties of all samples were similar, despite their different topology. The melting points of all polymers **1** to **3** were in the range of 48−54 °C (see Supporting Information), with similar melting enthalpies $\Delta H = 61-79$ J/g; glass transitions (T_g) were observed at −15 to −25 °C. This is not unexpected, since the linear material is atactic and the alkyl side chains determine the crystallization behavior for the linear and hyperbranched analogues.

Our results underline the crucial role of the hyperbranched topology and the resulting solution conformation in supramolecular guest encapsulation and phase transfer. We conclude that the unusually compact ("collapsed") structure assumed by hyperbranched core−shell amphiphiles in apolar media is responsible for the formation of a hydrophilic compartment, capable of irreversibly taking up guest molecules.

Acknowledgment. H.K and H.F. are grateful for fellowships from the Fonds der Chem. Industrie. S.-E.S. acknowledges an Alexander von Humboldt fellowship.

Supporting Information Available: Synthetic procedures and additional supporting data (UV−vis spectra, NMR and DSC data) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Jikei, M.; Kakimoto, M. *Prog. Polym. Sci.* **2001**, *26*, 1233. (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Synthesis, Perspectives*; VCH: Weinheim, 2001. (c) Kim, Y. H. *J. Polym. Sci., Polym. Chem. Ed.* **1998**, *36*, 1685. (d) Voit, B. I. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 2505. (e) Sunder, A.; Heinemann, J.; Frey, H. *Chem. Eur. J.* **2000**, *6*, 2499. (f) Markoski, L. J.; Moore, J. S.; Sendijarevic, I.; McHugh, A. J. *Macromolecules* **2001**, *34*, 2695.

(2) (a) Hawker, C. J.; Malmström, E. E.; Curtis, W. F.; Kampf, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 9903. (b) Harth, E. M.; Hecht, S.; Helms, B.; Malmström; E. E.; Fréchet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 3926.

(3) Supramolecular properties of dendrimers: (a) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74. (b) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 18. (c) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884. (d) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665. (e) Zeng, F. W.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681.

(4) (a) Jansen, J. F. G. A.; Meijer, E. W.; de Brabander-van den Berg, E. M. M. *J. Am. Chem. Soc.* **1995**, *117*, 4417. (b) Schenning, A. P. H. J.; Elissen-Román, C.; Weener, J.-W.; Baars, M. W. P. L.; van der Gaast, S. J.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 8199. (c) Gopidas, K. R.; Leheny, A. R.; Gaminati, G.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 7335. (d) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1278. (e) Stevelmans, S.; van Hest, J. C. M.; Jansen, J. F. G. A.; van-Boxtel, D. A. F. J.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *J. Am. Chem.. Soc.* **1996**, *118*, 7398.

(5) (a) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Saunders: M. J.; Grossman, S. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1178. (b) Jansen, J. F. G. A.; De Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226.

(6) Sunder, A.; Hanselmann, H.; Frey, H.; Mülhaupt, R. *Macromolecules* **1999**, *32*, 4240.

(7) (a) Sunder, A.; Krämer, M.; Hanselmann, R.; Mülhaupt, R.; Frey, H. *Angew. Chem.* **1999**, *111*, 3758; *Angew. Chem., Int. Ed.* **1999**, *38*, 3552.

(8) (a) Mecking, S.; Thomann, R.; Frey, H.; Sunder, A. *Macromolecules* **2000**, *33*, 3958. (b) Slagt, M. Q.; Stiriba, S.-E.; Klein Gebbink, R. J. M.; Kautz, H.; Frey, H.; van Koten, G. *Macromolecules* **2002**, *35*, 5734.

(9) Anton, P.; Köberle, P.; Laschewsky, A. *Makromol. Chem.* **1993**, *194*, 1.

(10) Nomenclature: hyperbranched molecular nanocapsule; $P(G_xCY_\alpha)$, $x = DP_n$ of polyglycerol, Y = length of respective alkyl chain, i.e., the number of carbon atoms, α = degree of alkyl substitution per hydroxy group. The same nomenclature was used for the linear esterified $LP(G_xCY_\alpha)$.

(11) Taton, D.; Le Borgne, A.; Sepulchre, M.; Spassky, N. *Macromol. Chem. Phys.* **1994**, *195*, 139.

(12) Elias, H.-G. *An Introduction to Polymer Science*, VCH: Weinheim, 1997; Chapter 5.8.

JA026835M