Self-association of poly(aramide) dendrimers

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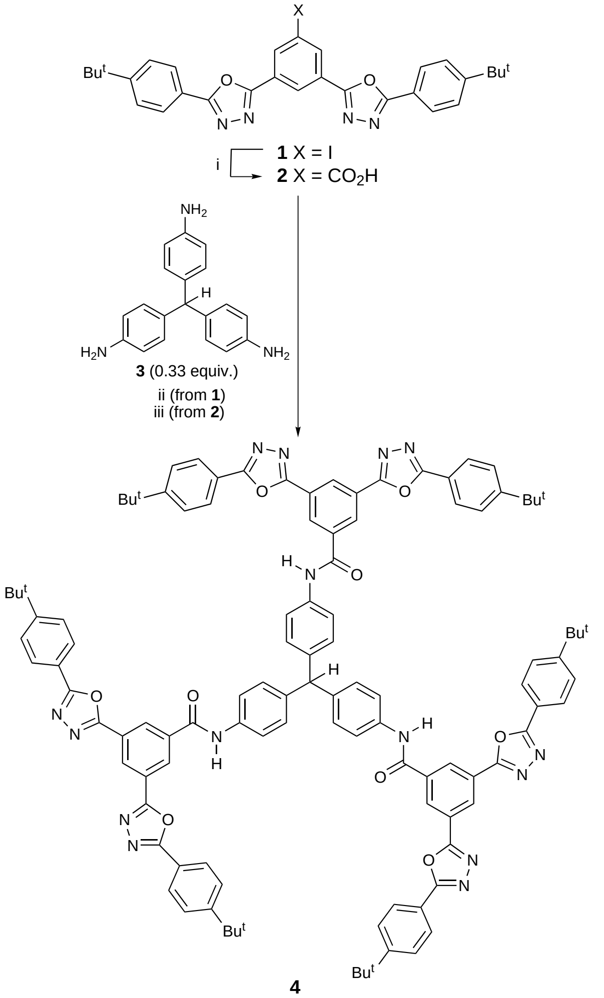
Two poly(aramide) dendrimers, which possess electron-deficient 1,3,4-oxadiazole and aromatic systems linked by amide units to a triphenylmethane core, strongly self-associate in chloroform solution through hydrogen bonding.

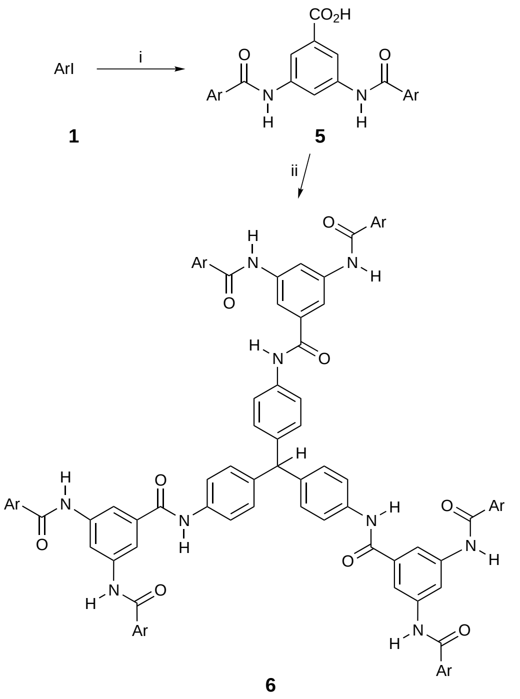
During the last decade, dendrimers with highly branched, spherical structures have attracted much attention.[1] They often possess unique properties, such as unusually good solubility. Linear poly(aramide)s, for example, are well-known high-performance fibre materials which owe their high tensile strength to a large degree of hydrogen bonding between aligned polymer chains; however, these polycondensates dissolve only in highly polar solvents such as concentrated sulfuric acid. In contrast, the few hitherto known dendritic or hyperbranched poly(aramide)s are soluble in DMF, DMSO and THF, yet the attempts towards their synthesis were hampered by side reactions.[2,3] We have recently embarked on a programme to synthesise dendrimers containing 1,3,4-oxadiazole systems.[4] These heterocycles are notable for their potential application as electron-transporting materials in electroluminescent devices based on organic fluorescent dyes and polymers.[5] The star-branched and dendritic derivatives with ⩾3 oxadiazoles per molecule dissolve well in chlorinated and aromatic solvents, form amorphous glasses[6,7] and tend towards π-stacking in solution.[4] We now report the synthesis of oxadiazole-containing poly(aramide) dendrimers that are soluble in organic solvents such as chloroform. So far, our efforts have concentrated on structures with a triphenylmethane core, starting with triamine **3**.[8]

Palladium-catalysed carbonylations[9] form the key step in the syntheses of dendritic poly(aramide)s **4** and **6**. Branched compound **4** is thus obtained in a single step from aryl iodide **1**, **3** and carbon monoxide with *N*-methyl-2-pyrrolidone (NMP) as solvent, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base and $PdCl_2$–$Ph_2P(m\text{-}C_6H_4SO_3Na)$[10] as catalyst (Scheme 1). The seven-component reaction furnished **4** in 45% yield after purification by column chromatography.† However, it proved very difficult to remove the last traces of the NMP residues, and we therefore sought a different method that avoided the use of a high-boiling solvent in the last step of the synthesis. Conversion of **1** into carboxylic acid **2** was accomplished by another palladium-catalysed carbonylation. In a subsequent step, acid **2** and triamine **3** were coupled with triphenyl phosphite[11] in pyridine. Carbonylation reactions were also effective for the preparation of acid **5** and had the particular advantage that no protecting groups were required. Coupling of the acid with **3** finally furnished **6** (Scheme 2).

As usually for dendrimers, solubility is mainly determined by the substitutents at the periphery (in our case, these are *tert*-butyl substituted aromatic systems) whereas the amide groups in the centre of **4** and **6** induce hydrogen-bonding interactions. In fact, the solubility of dendrimer **4** in chloroform extends to 50–60 mg ml^{-1}. It was at first surprising to find that **6**, which has nine amide groups, dissolves with even more ease in chloroform (over 200 mg ml^{-1}). This is one of the advantages of the branched dendrimer structure.[1,2] While a linear aramide structure in poly(aramide)s has a detrimental effect on solubility, the higher degree of branching in **6** counteracts the solvophobic effect of the extra amide groups. The ^1H NMR spectra of **4** and **6** depend strongly on concentration, temperature and solvent while lineshapes are not influenced by the NMR frequency. This rules out dynamic processes and is a strong indication of self-association.[12] The ^1H NMR signals of **4** in $CDCl_3$ are all broad and without fine structure. The fact that they become sharp on addition of $[^2H_6]$DMSO (15%) underlines that hydrogen-bonding is responsible for the self-association of **4**. We estimated the association constant K_a of **4** in $CDCl_3$ by a dilution experiment. A decrease in concentration below 10^{-3} mol dm^{-3} led to a significant increase in resolution of the ^1H NMR signals. Most chemical shifts were only slightly dependent on concentration ($\Delta\delta \leqslant 0.25$) with the exception of the NH singlet. In the concentration range investigated (10^{-1} to 10^{-3} mol dm^{-3}), δ_{NH} varied from 9.91 to 9.11 and allowed K_a



Scheme 1 *Reagents and conditions:* i, $LiOH{\cdot}H_2O$ (2 equiv.), $PdCl_2$ (0.03 equiv.), $Ph_2P(m\text{-}C_6H_4SO_3Na)$ (0.09 equiv.), NMP, CO, 100 °C, 1–2 d, then HCl, 79–95%; ii, $PdCl_2$ (0.03 equiv.), $Ph_2P(m\text{-}C_6H_4SO_3Na)$ (0.09 equiv.), DBU (1.2 equiv.), NMP, CO, 100 °C, 1–2 d, then HCl, 31%; iii, $P(OPh)_3$ (1.2 equiv), pyridine, 100 °C, 12 h, then HCl, 45%



Scheme 2 *Reagents and conditions:* i, 3,5-diaminobenzoic acid (0.5 equiv.), $PdCl_2$ (0.6 equiv.), $Ph_2P(m\text{-}C_6H_4SO_3Na)$ (0.18 equiv.), DBU (1.8 equiv.), NMP, CO, 100 °C, 4 d, then HCl, 38%; ii, **3** (0.33 equiv.), $P(OPh)_3$ (1.2 equiv.), pyridine, 100 °C, 12 h, then HCl, 37%

to be estimated to 790 ± 100 dm^3 mol^{-1} in dry chloroform at 30 °C, assuming the isodesmic model of indefinite self-association.[13] Hydrogen bonds weaken also at higher temperature: the ^1H NMR spectrum of a 0.005 mol dm^{-3} solution of **4** in $CDCl_3$–$C_2D_2Cl_4$ (1:2) revealed sharp signals and the expected multiplicity pattern for the aromatic protons upon raising the temperature to 80 °C. Vapour-pressure osmometry (VPO) studies in chloroform at 30 °C gave evidence of an association degree $\geqslant 4$ and a number average molar mass exceeding 3500 g mol^{-1} (over twice as high as expected for non-associated **4**) at concentrations $\geqslant 0.02$ mol dm^{-3}. At comparatively low concentrations, a significant amount of **4** is present in solution in the form of higher oligomers. Although self-association generally counteracts solubility, the branched structure of **4** successfully suppresses precipitation of the compound. Only after chromatography could a small amount of **4** be induced to crystallise from a CH_2Cl_2–MeOH.

Association becomes even more dominant for **6** with its nine amide groups. The ^1H NMR spectrum of the dendrimer in $CDCl_3$ is characterised by broad signals, and even the *tert*-butyl 'singlet' has a linewidth of $\Delta\delta \approx 0.4$ (at 0.002 mol dm^{-3}) at half maximum. Addition of $[^2H_6]$DMSO no longer suffices to break up all hydrogen bonds. In fact, this demands the addition of a much more polar cosolvent such as trifluoroacetic acid. The remarkably strong association is also deduced from the ^1H NMR spectrum of **6** in $C_2D_2Cl_4$ (0.01 mol dm^{-3}) at 138 °C, which still displays broadened signals for the aromatic protons and a complicated pattern for the *tert*-butyl protons between δ 0.95 and 1.50. It seems unlikely that all amide groups will be involved in hydrogen bonding because the propeller configuration of the triphenylmethane[14] core and the disordered structure of the branched periphery prevent such a fit. Nevertheless, a larger number of amide groups per dendrimer molecule enhance the probability of multiple interactions and therefore contributes to an increased association constant. In addition, the electron-deficient oxadiazole and aromatic systems also take part in aromatic–aromatic interactions, judging from the upfield ^1H NMR shifts of several aromatic proton signals.[15]

At first glance the molar masses of dendrimers **4** and **6** seem to be comparitively low, yet the tendency of these compounds to strongly self-associate in solution makes them behave like polymers, as is apparent by an increased viscosity and effective molar mass even in dilute solutions. Whereas polymers suffer from a lack of purification methods that makes it difficult to remedy any incorporated structural defects, dendrimers can be much more easily purified. We expect that self-associating poly(aramide) dendrimers with solubilising and electroactive functional groups at the periphery will have promising material properties, which are the subject of further investigations.

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and Professor G. Wulff for generous support, Dr H. Luftmann (University of Münster) for MALDI-TOF MS measurements, and Ms H. Fürtges for assistance in the preparation of starting materials.

Footnotes

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[†] All compounds were characterised by microanalysis, IR, NMR and mass spectroscopy. *Selected data* for **4**: ^1H NMR (500 MHz, $CDCl_3$–$[^2H_6]$DMSO, 6:1) 1.40 (s, CH_3), 5.63 (s, 1 H, Ar_3CH), 7.24, 7.88 [AA'XX', 12 H, $(C_6H_4)_3C$], 7.60, 8.11 (AA'XX', 24 H, $Bu^tC_6H_4$), 8.96 (t, *J* 1.6 Hz, 3 H), 8.99 (d, 6 H, C_6H_3), 10.50 (s, NH); R_f (CH_2Cl_2–MeOH, 15:1) 0.75. For **6**: ^1H NMR (500 MHz, $CDCl_3$–CF_3CO_2D, 6:1) 1.38 (s, CH_3), 5.71 (s, 1 H, Ar_3CH), 7.27, 7.63 [AA'XX', $(C_6H_4)_3C$], 7.67, 8.16 (AA'XX', $Bu^tC_6H_4$), 8.37 (br s, 6 H), 8.68 [br s, 3 H, $(CONH)_2C_6H_3CO$], 9.18 (br s, 2 H), 9.23 (br s, 1 H, C_6H_3); R_f(CH_2Cl_2–MeOH, 9:1) 0.5.

References

1 For a recent monograph on dendrimers, see G. R. Newkome, C. N. Moorefield and F. Vögtle, *Dendritic Molecules: Concepts, Synthesis, Perspectives,* VCH, Weinheim, 1996.
2 S. C. E. Backson, P. M. Bayliff, W. J. Feast, A. M. Kenwright, D. Parker and R. W. Richards, *Macromol. Symp.,* 1994, **77**, 1.
3 Y. H. Kim, *J. Am. Chem. Soc.,* 1992, **114**, 4947.
4 A. Kraft, *Chem. Commun.,* 1996, 77.
5 Application of 1,3,4-oxadiazole derivatives in electroluminescent devices: Y. Hamada, C. Adachi, T. Tsutsui and S. Saito, *Jpn. J. Appl. Phys.,* 1992, **31**, 1812; A. R. Brown, D. D. C. Bradley, J. H. Burroughes, R. H. Friend, N. C. Greenham, P. L. Burn, A. B. Holmes and A. Kraft, *Appl. Phys. Lett.,* 1992, **61**, 2793.
6 X.-C. Li, A. Kraft, R. Cervini, G. C. W. Spencer, F. Cacialli, R. H. Friend, J. Grüner, A. B. Holmes, J. C. DeMello and S. C. Moratti, *Mater. Res. Soc. Symp. Proc.,* 1996, **413**, 13.
7 J. Bettenhausen and P. Strohriegl, *Adv. Mater.* 1996, **8**, 507; J. Bettenhausen and P. Strohriegl, *Makromol. Chem., Commun.,* 1996, **17**, 623.
8 D. Hellwinkel and H. Fritsch, *Chem. Ber.,* 1990, **123**, 2207.
9 For other syntheses of poly(aramide)s by palladium-catalysed carbonylations, see M. Yoneyama, M. Kakimoto and Y. Imai, *Macromolecules,* 1988, **21**, 1908; S. R. Turner, R. J. Perry and R. W. Blevins, *Macromolecules,* 1992, **25**, 4819; V. R. Reichert and L. J. Mathias, *Macromolecules,* 1994, **27**, 7024.
10 S. Ahrland, J. Chatt, N. R. Davies and A. A. Williams, *J. Chem. Soc.,* 1958, 276.
11 N. Yamazaki, M. Matsumoto and F. Higashi, *J. Polym. Sci., Polym. Chem. Ed.,* 1975, **13**, 1373.
12 Until now, dendrimer–dendrimer interactions involved mainly micelle formation, aggregation or self-assembly in solution, and liquid-crystalline phase transition in the absence of solvent: G. R. Newkome, C. N. Moorefield, G. R. Baker, R. K. Behera, G. H. Escamillia and M. J. Saunders, *Angew. Chem., Int. Ed. Engl.,* 1992, **31**, 917; J. M. J. Fréchet and I. Gitsov, *Macromol. Symp.,* 1995, **98**, 441; V. Percec, P. Chu, G. Ungar and J. Zhou, *J. Am. Chem. Soc.,* 1995, **117**, 11441; J. C. M. van Hest, D. A. P. Delnoye, M. W. P. L. Baars, C. Elissen-Román, M. H. P. van Genderen and E. W. Meijer, *Chem. Eur. J.,* 1996, **2**, 1616; S. C. Zimmerman, F. Zeng, D. E. C. Reichert and S. V. Kolotuchin, *Science,* 1996, **271**, 1095.
13 R. B. Martin, *Chem. Rev.,* 1996, **96**, 3043.
14 N. Veldman, A. L. Spek, J. J. H. Schlotter, J. W. Zwikker and L. W. Jenneskens, *Acta Crystallogr., Sect. C,* 1996, **52**, 174.
15 For hydrogen-bonding in aramides and attractive π-interactions between electron-poor aromatic compounds, see A. P. Bisson and C. A. Hunter, *Chem. Commun.,* 1996, 1723; C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.,* 1990, **112**, 5525.

Received in Cambridge, UK, 6th May 1997; 7/03072J