Lyotropic Liquid Crystalline Hyperbranched Aromatic Polyamides[†]

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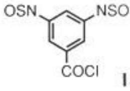
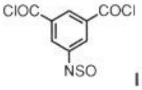
New classes of highly branched substances have attracted increasing attention due to the expectation that their unique spherical structures will impart unusual properties.[1] These materials demonstrate characteristics such as supermolecular assembly,[2] micellar properties,[3] and behavior as molecular level ball bearings in viscous media.[4] We report here new hyperbranched aromatic polyamides which exhibit lyotropic properties. While liquid crystalline (LC) properties of linear "rigid-rod" type aromatic polymers are well known,[5] LC formation by highly branched spherical shaped polymers has not been reported.[6]

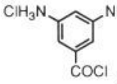
The polymers were prepared from monomers **I** and **II** in an amide solvent at low temperature. The sulfinyl amino acid chlorides (**Ia**, **IIa**), prepared from the aromatic amino acids and thionyl chloride, were treated with dry hydrochloric acid to give amino acid chloride hydrochlorides (**Ib**, **IIb**).[7] In an amide solvent, the hydrochloride was neutralized to give the free amine, allowing condensation polymerization to take place (method A).[8] Alternatively, the sulfinyl amino acid chloride derivatives were polymerized in the presence of 1 equiv of water (method B). Polymer **IV**, prepared from monomer **II** in *N*-methylpyrrolidinone (NMP), precipitated well in water, but polymer **III**, made from monomer **I**, was water soluble and precipitated only when base or salt was added to the solution. The methyl ester of polymer **IV** was prepared by addition of MeOH at the end of the reaction. Better defined samples of these highly branched polymers should be obtainable by a stepwise synthesis, either divergent[1a,e,h,2a] or convergent.[1b–d,g] However, earlier attempts at stepwise synthesis was found difficult due to the low solubility of oligomeric intermediates.[9]



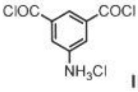
Ia



IIa



Ib



IIb

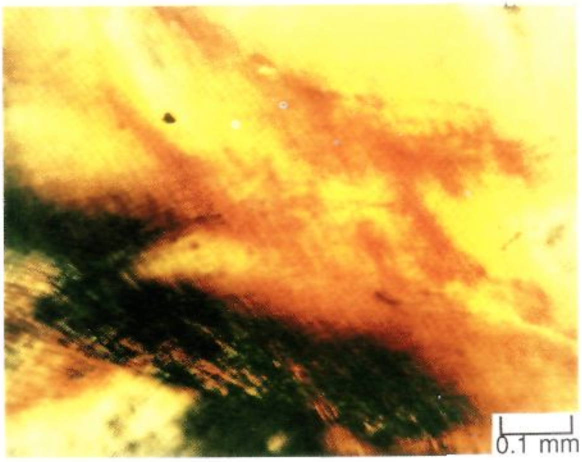
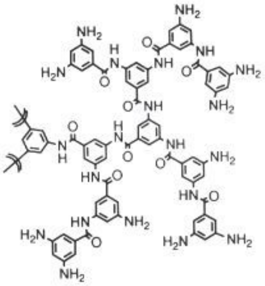
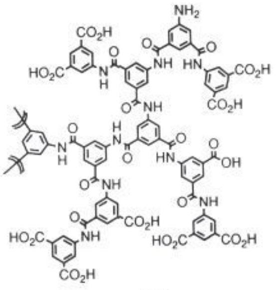


Figure 1. Polarized light optical microgram of 60 wt % polymer **IV** in *N*-methylpyrrolidinone. The sample was prepared by cold pressing the solution at 1000 psi.



III



IV

Polymers **III** and **IV** are soluble in amide solvents, such as *N*,*N*-dimethylacetamide (DMAC), *N*,*N*-dimethylformamide (DMF), and NMP. A major difference between these two polymers lies in the nature of the functional groups at the surface. An ideal polymerization of an AB$_x$ type monomer, in which only A reacts with B, will have $(x - 1)$DP + 1 B functional groups at the surface of the polymer, where DP is the degree of polymerization.[10] Thus, polymer **III** has DP + 1 NH$_2$ functional groups, whereas polymer **IV** has the same number of COOH groups. The acid generated during the polymerization converted the amine group of polymer **III** to the hydrochloride salt, which makes the polymer soluble in water. Unlike hyperbranched polyphenylene,[3] however, polymer **IV** was insoluble in aqueous alkali solution.

The polymer molecular weights were determined by gel permeation chromatography (GPC) using a DMAC/LiBr/H_3PO_4/THF[11] mixture as the carrier solvent. They ranged from 24 000 to 46 000 with polydispersities of 2.0–3.2 (polystyrene standards). However, in pure DMF as the carrier solvent, the exclusion volumes corresponded to 700 000–1 000 000 molecular weight. This indicates that the polymer forms aggregates in the absence of complexing ions, even in dilute solution. The aggre-

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[†] Contribution No. 6084.

(1) (a) Tomalia, D. A.; Naylor, A. M.; Goddard, III, W. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138 and references therein. (b) Hawker, C.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (c) *Ibid. J. Chem. Soc., Chem. Commun.* **1990**, 1010. (d) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4252. (e) Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 7077. (f) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043. (g) Miller, T. M.; Neeman, T. X. *Chem. Mater.* **1990**, *2*, 346. (h) Newkome, G. R.; Lin, X. *Macromolecules* **1991**, *24*, 1443.

(2) (a) Newkome, G. R.; Baker, G. R.; Saunders, M. J.; Russo, P. S.; Gupta, V.; Yao, Z.; Miller, J. E.; Bouillion, K. *J. Chem. Soc., Chem. Commun.* **1986**, 752. (b) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V.; Russo, P. S.; Saunders, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 849.

(3) (a) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592. (b) Tomalia, D. A.; Berry, V.; Hall, M.; Hedstrand, D. M. *Macromolecules* **1987**, *20*, 1164.

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(5) See, for example: (a) Flory, P. J. *Adv. Polym. Sci.* **1984**, *58*, 1. (b) Kwolek, S. L. In *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; Wiley: New York, 1987; Vol. 9, pp 1, 61. (c) Northolt, M. G.; Sikkema, D. J. *Adv. Polym. Sci.* **1990**, *98*, 115.

(6) See, however: Friberg, S. E.; Podzimek, M.; Tomalia, D. A.; Hedstrand, D. M. *Mol. Cryst. Liq. Cryst.* **1988**, *164*, 157.

(7) Kwolek, S. L.; Morgan, P. W.; Schaefgen, J. R.; Gulrich, L. W. *Macromolecules* **1977**, *10*, 1390.

(8) A representative polymerization procedure from the acid chloride is as follows. To 200 mL of NMP containing 15.6 g of $CaCl_2$ was added 6.76 g of 3-aminoisophthaloyl chloride hydrogen chloride at 0 °C, which were then reacted for 2 h at room temperature. Polymer **IV** was precipitated from water: ^{1}H NMR (DMF–d_7, ppm) 8.4–8.6 (br m, 1 H), 9.9 (br, 2 H), 11.1 (br, 1 H); ^{13}C NMR (DMF-d_7, ppm) 122.8, 123.8, 124.3, 124.6, 125.0, 125.6, 125.7, 126.2, 132.8, 136.5, 136.7, 140.9, 166.2, 167.5; IR (cm^{-1}) 1705 (*CO*OH), 1660 (amide I), 1600 (amide II). Polymer **III**: ^{1}H NMR (DMF-d_7) 6.05 (d, 0.5 H), 6.35–6.4 (d, 1 H), 6.8–6.9 (d, 1 H), 7.3–7.5 (d, 2 H), 8.1 (broad, 1 H), 9.6–10.3 (t, 2 H); ^{13}C NMR (DMF-d_7, ppm) 105.2, 109.5, 110.2, 116.4, 136.8, 141.6, 149.9, 163.1, 169.8; IR (cm^{-1}) 1650 (amide I), 1600 (amide II and NH$_2$).

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Table I. Solution Properties of Polymer **IV**

	polymerization conditions	molecular weight by GPC: DMAC/LiBr/ H_3PO_4/THF	molecular weight by GPC: DMF	clearing point of 50 wt % NMP lyotropic solution (°C)
IVa	method A with $CaCl_2$	46 000	1 030 000	>150
IVb	method A without added salt	30 600	872 000	>150
IVc	method A without $CaCl_2$ quenched with MeOH	23 500	741 000	70–80
IVd	method B with $CaCl_2$	–	–	>150
IVe	method A quenched with $Ca(OH)_2$	insoluble	insoluble	

gation is not due to the end group effect, because the methyl ester of this polymer shows the same degree of association.

Amide solutions containing more than 40 wt % of polymer **IV** exhibit nematic phase LC texture under a polarizing microscope at room temperature (Figure 1). A 60 wt % solution is a hard gel under static conditions, but becomes more fluid as shear force is applied. These solutions did not lose birefringence up to 150 °C. The methyl ester of this polymer also showed birefringence at room temperature, but became isotropic at about 70 °C (Table I). The solution regains birefringence after standing for approximately 1 day at room temperature. This behavior may be related to the polymer's propensity to form aggregates in amide solvents as observed in the GPC experiment. Indeed, these polymers showed no birefringence in amide solvents containing as little as 0.1 wt % $CaCl_2$. On the other hand, polymer **III** did not show birefringence under these conditions. We cannot offer a clear explanation for our observation at this point, but we are investigating the effect of aggregation and the end functional groups on the lyotropic properties.[12]

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(12) V. Percec and his associates at Case Western Reserve University, Cleveland, OH, communicated to us that they have found a hyperbranched polymer consisting of flexible chains and aromatic rings which exhibits the thermotropic LC property. Unlike **IV** their polymer seems to comply with Flory's theory (see ref 5) for LC formation in spite of its highly branched structure.