

# Molecular design of novel liquid crystalline polymers with complex architecture: Macrocyclics and dendrimers

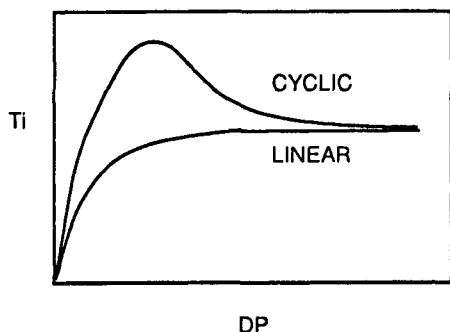
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**Abstract:** This paper discusses recent results from our laboratory on the molecular design of two novel classes of liquid crystals with complex architecture, i.e., supramolecular quasi-rigid-rods generated from collapsed macrocyclics and dendrimers based on flexible AB<sub>2</sub> monomers which exhibit conformational isomerism.

## Supramolecular Quasi-Rigid-Rods from Collapsed Macrocyclics

Soon after the discovery of liquid crystals (1) it was recognized that rigid rod-like and disc-like compounds provide the most suitable molecular architectures which lead to liquid crystalline mesophases (2a). One hundred years later, the discussion on the molecular structure-properties relationship in the field of liquid crystals is still focused on the same two architectures and on a few less conventional variants of them (2b-e). The same statement is valid for the field of macromolecular and supramolecular liquid crystals in which both linear main chain and side-chain liquid crystalline polymers containing single rod-like and disc-like or various combinations of dissimilar mesogens were elaborated (3). Liquid crystals based on cyclic oligosiloxanes containing mesogenic side groups were reported both from our and other laboratories (4).



**Fig. 1:** The theoretical and experimental dependence of the isotropization temperature ( $T_i$ ) of cyclic and linear main-chain liquid crystalline polymers on their degree of polymerization (DP). Both  $T_i$  and DP are in arbitrary units.

The membranes of archaeobacteria, i.e., extremophile microorganisms which proliferate in extreme environments such as high temperature, acid, alkali or high salt concentration, are formed from macrocyclic oligoether lipids since these lipids are more stable than the corresponding linear ones (5a). In 1992 it has been demonstrated that macrocyclic lipids display a thermotropic mesophase (5b,c) and very recently that they generate highly stable liposomes (5d).

Independently, in 1992, we have predicted and demonstrated that certain sizes of low-molar mass macrocyclics which are homologues of main chain liquid crystalline polymers based on conformationally flexible rod-like mesogens should and do exhibit a higher ability to generate liquid crystalline phases than do their low-molar-mass linear and both their linear and cyclic high molecular mass compounds (Fig. 1) (6). The trend from Fig. 1 is due to the fact that macrocyclics of a certain size which contain at least a minimum extent of ring strain and a proper combination of spacer and mesogenic lengths based on which they can generate a liquid crystalline phase, should have a lower entropy and therefore, must display higher transition temperatures (7) than the corresponding high molar mass linear and cyclic compounds. Scheme 1 outlines the *anti* and *gauche* conformers of 1-(4-hydroxybiphenyl-4-yl)-2-(4-hydroxyphenyl)butane (TPB) and the macrocyclization of TPB with  $\alpha,\omega$ -dibromoalkanes by a high dilution phase transfer catalyzed polyetherification. Optimum reaction conditions yield either the regioirregular linear polymer TPB-(l)X(8) or a mixture of up to five sizes of regioirregular macrocyclics TPB-(c)X(z) which can be separated (where: l stands for linear, X represents the number of methylenic units in the spacer, c stands for cyclic and z is the

degree of oligomerization of the macrocyclic compound). Both the regioirregular TPB-(l)X and TPB-(c)X(z) with  $X = 2$  to  $20$  and  $z = 1$  to  $5$  were synthesized and their phase behavior was investigated. Questions like: what is the shorter spacer  $X$  and the minimum ring size  $z$  of TPB-(c)X(z) which displays a liquid crystalline phase? what is the lowest size of the macrocyclic which displays a liquid crystalline phase whose isotropization temperature is higher than that of its linear high molar mass homologue? (6,9a,b) what is the probability of transforming kinetically prohibited (9) and/or kinetically controlled (9d) mesophases of the linear polymer into enantiotropic mesophases via cyclization? what is the ability to generate noncrystallizable macrocyclics with a high glass transition temperature and a broad range of temperature of the mesophase? (9e) what is the dependence of the phase transition temperatures of a certain macrocyclic on its spacer length  $X$  and how does it compare with that of the corresponding linear polymer? (9b) were addressed, answered and explained.

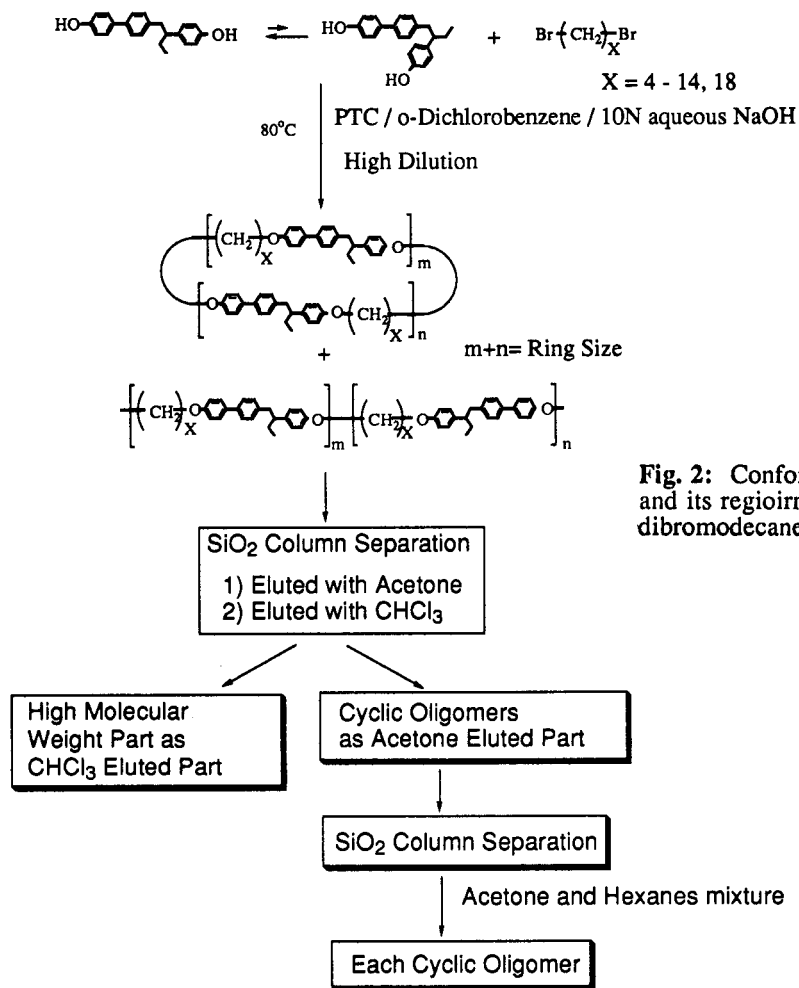
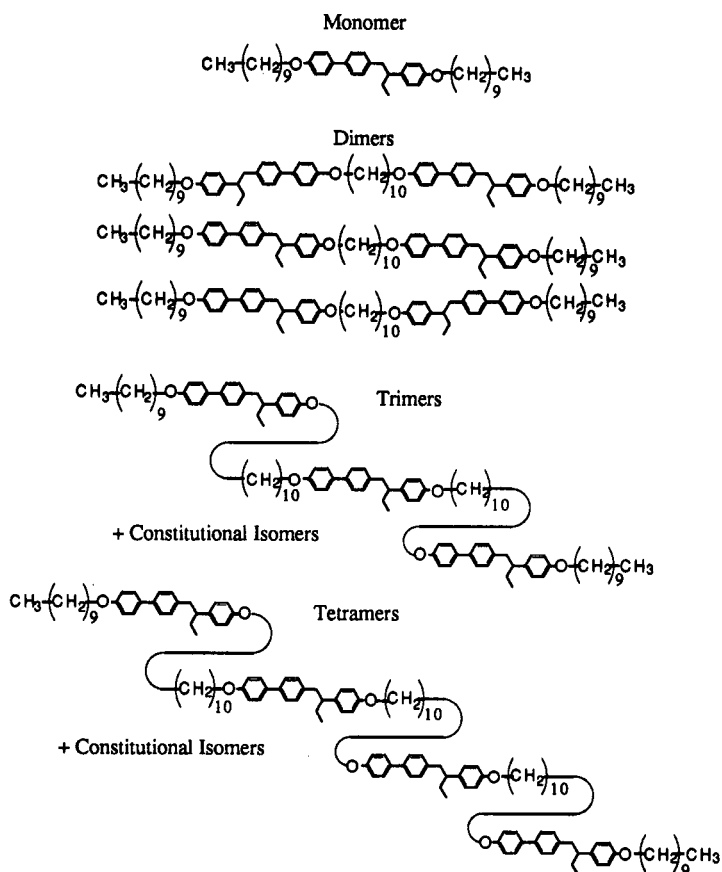
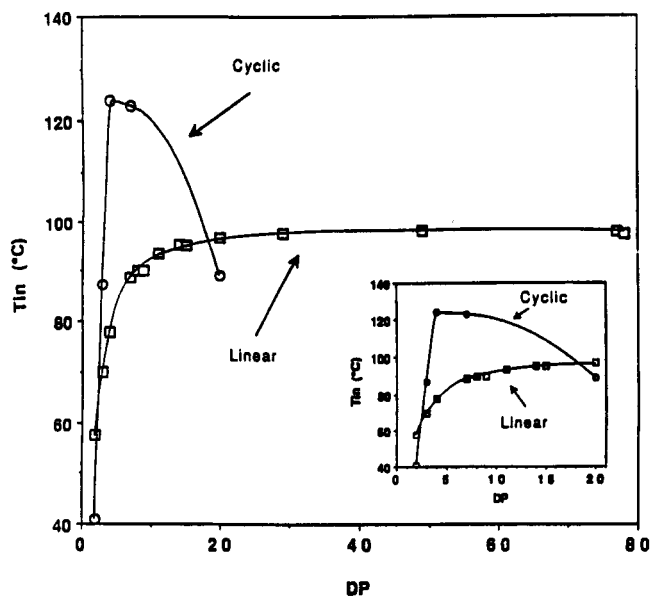


Fig. 2: Conformational isomerism of TPB and its regioirregular cyclization with 1,10-dibromodecane under high-dilution conditions.

Figure 2 outlines the synthesis of macrocyclic and linear polyethers based on TPB and  $\alpha,\omega$ -dibromoalkanes. The structure of these macrocyclics was confirmed by a combination of 300 MHz 1-D and 2-D  $^1\text{H-NMR}$  experiments and by molecular weight determination (6).  $^1\text{H-NMR}$  spectroscopy was used to demonstrate that ring strain is released above the size of pentamer. The phase behavior of individual regioirregular linear monomer, dimer, trimer, tetramer TPB-(l)10 (Fig. 3) and that of the high molecular weight linear polymers with narrow molecular weight distribution TPB-(l)10 is compared to that of the TPB-(c)(10)z ( $z = 1$  to  $5$ ) in Fig. 4 (10). Both the linear and cyclic compounds from Fig. 4 exhibit a nematic mesophase. The linear dimer has a higher isotropization temperature than the cyclic one. However, the cyclic trimer displays a much higher ability to form a nematic mesophase than the corresponding linear trimer. At the same time, the cyclic tetramer and pentamer exhibit much higher abilities to form nematic mesophases than even the very high molecular weight linear polymer. *These results demonstrate that at least in the case of the macrocyclic compounds based on TPB and 1,10-dibromodecane, the tetramer and pentamer and not the linear high molar mass polymers exhibit the highest tendency to form nematic mesophases.*



**Fig. 3:** The structures of the linear regioirregular model compounds of TPB-(I)10.



**Fig. 4:** Dependence of the isotropic-nematic ( $T_{in}$ ) transition temperatures of regioirregular linear (□) and macrocyclic (○) oligomers and polymers of TPB-(I)10 on their degree of polymerization.

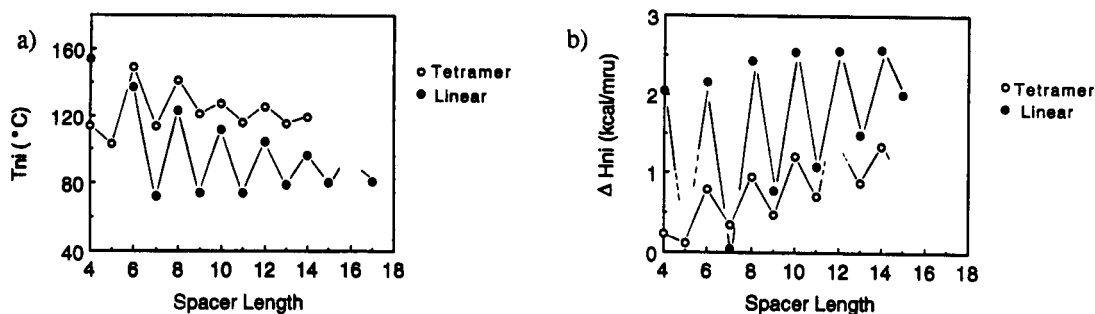


Fig. 5: The dependence of the isotropic-nematic transition temperature ( $T_{ni}$ ) (a) and of its associated enthalpy changes ( $\Delta H_{ni}$ ) (b) of regioirregular TPB-(c)X(4) (cyclic tetramer) and TPB-(l)X (high molecular weight linear polymer) on spacer length (X).

Figure 5a compares the isotropization temperatures ( $T_{ni}$ ) of TPB-(c)10(4) and of TPB-(l)10 as a function of the number of methylenic units in the spacer. All TPB-(c)10(4) have higher  $T_{ni}$  values than the corresponding linear polymers. The  $\Delta H_{ni}$  values of  $T_{ni}$  are plotted in Fig. 5b.  $\Delta H_{ni}$  of cyclics are lower than of the corresponding linear polymers since the difference between the entropies of a macrocyclic in isotropic and nematic phases is lower than the corresponding parameter of the linear polymer. The odd-even dependencies of  $T_{ni}$  and  $\Delta H_{ni}$  of cyclic tetramers and linear compounds are similar.

Figure 6a plots the thermal transitions of TPB-(c)10(3) and Fig. 6b their  $\Delta H_{ni}$  values. Both sets of data of TPB-(c)10(3) (Fig. 6) are different from those of TPB-(c)10(4) (Fig. 5).  $T_{ni}$  values of cyclic trimers show a very weak odd-even dependence of spacer length. However, this dependence (Fig. 6a) follows the reversed trend of the data from Fig. 5a.  $T_{ni}$  of cyclic trimers are increasing with the increase in spacer length while the same data of cyclic tetramers are decreasing. The cyclic trimers show higher  $T_{ni}$  for odd spacer length while cyclic tetramers and linear polymers for even spacer length. Both the  $T_{ni}$  and  $\Delta H_{ni}$  values from Fig. 6 demonstrate that the rigidity of cyclic trimers increases with the increase in spacer length. Therefore, while cyclic tetramers resemble the behavior of linear polymers, cyclic trimers represent a completely different class of LC. Finally, cyclic trimers with very short and very long spacers exhibit, in addition to the nematic mesophase, a smectic A ( $S_A$ ) phase (Fig. 6a). Regardless of the spacer length, the layer of the  $S_A$  phase of the cyclic trimers is equal to  $1.5 \times (L_m + L_s)$  in which  $L_m$  is the length of the *anti* conformer of TPB while  $L_s$  is equal to the length of the flexible spacer in its fully extended all *trans* conformation (Fig. 7). A trimer conformation like the middle right side of Fig. 7 requires that  $2L_m + L_s = 2 \times (L_s - 2.5) + L_m$  where  $2.5 \text{ \AA}$  is the minimum length of the  $180^\circ \text{C}$  turn in fold which is generated by two carbon atoms. Under these requirements the shorter spacer length ( $L_s$ ) which can accommodate such a structure is equal or longer than  $L_m$ , i.e.,  $L_s \geq L_m$ . At shorter spacer lengths a  $S_A$  phase can be found only when one TPB is in its gauche conformation and it is part of the fold (middle left trimer in Fig. 7) (11). Some experiments with macrocyclics based on enantiomerically enriched TPB suggest that intracyclic heterochiral recognition may have a contribution to the architecture of the larger macrocyclics in the nematic phase (12) and that a superhelical shape is not excluded. In addition, the nematic phase of TPB-(c)9(3) seems to be biaxial (13).

All these results suggest that in their liquid crystalline phase these compounds are *supramolecular rigid-rods generated from collapsed macrocyclics* (Fig. 8). This novel class of liquid crystals has recently received interest in other laboratories (14) and opens numerous avenues for the design of new macromolecular and supramolecular architectures based on liquid crystalline macrocyclic building blocks.

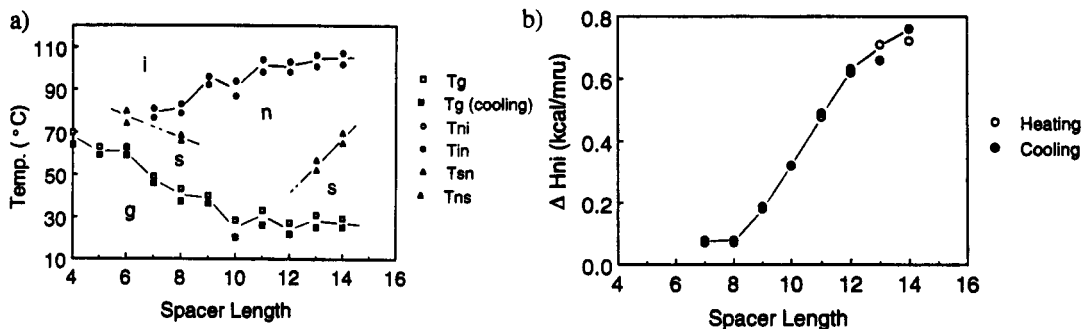


Fig. 6: The dependence of the various transition temperatures (a) and of the enthalpy changes (b) associated with the nematic-isotropic ( $\Delta H_{ni}$ ) transition temperatures of regioirregular TPB-(c)X(3) (cyclic trimer) versus spacer length (X).

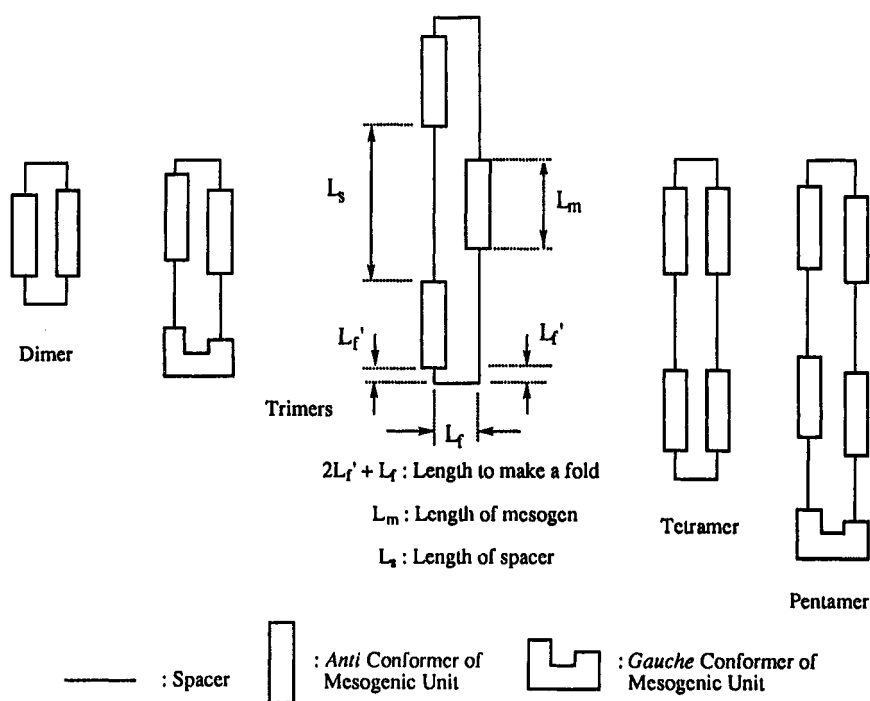


Fig. 7: The ideal architecture of cyclic oligomers (dimer to pentamer) in the crystalline and liquid crystalline phases.

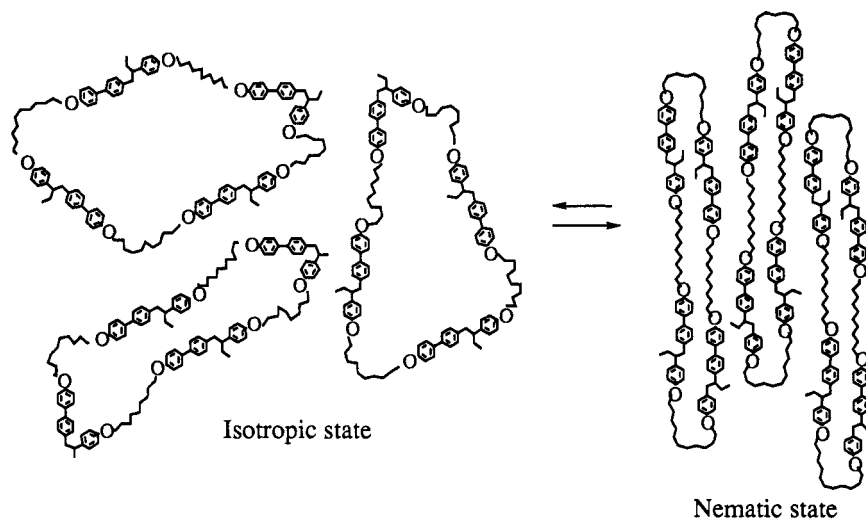


Fig. 8: Schematic representation of the suggested mechanism for the isotropic-nematic transition of TPB-(c)X(4).

### Dendrimeric Liquid Crystals

The synthesis and characterization of hyperbranched polymers and of dendrimers which are prepared via convergent or divergent approaches was extensively reviewed (15). The first examples of thermotropic hyperbranched polymers with disc-like mesogen (16) and rod-like flexible mesogens based on conformational isomerism (17,18) were reported from our laboratory. Independent from our work, Kim (19) reported the preparation of the first lyotropic hyperbranched polymers and more recently Ringsdorf et al (20) the first examples of thermotropic cholesteric hyperbranched polymers. The concept of "willow-like" hyperbranched thermotropic liquid crystals, the driving force behind our research and the most recent

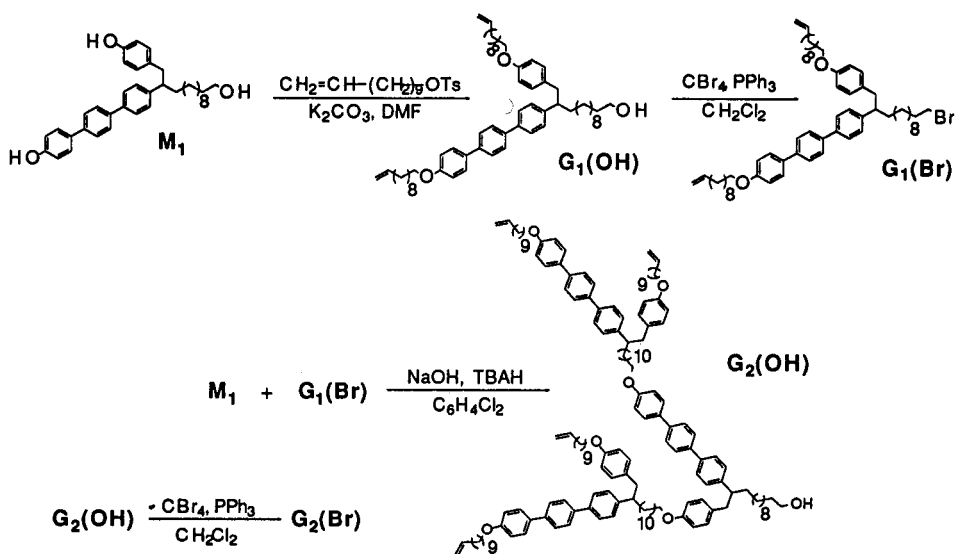


Fig. 9: Synthesis of G<sub>2</sub>(OH) and G<sub>2</sub>(Br).

developments in this field as well as the synthetic limitations of our method were recently discussed in detail (18). Here we will mention only briefly the synthetic strategy used for the preparation of the first examples of dendrimeric liquid crystals via a convergent method and describe some preliminary data on the similarities and differences between hyperbranched and dendrimeric liquid crystals. The AB<sub>2</sub> monomer M<sub>1</sub> (Fig. 9) was designed to synthesize the four generations of dendrons G<sub>1</sub>(OH), G<sub>1</sub>(Br) to G<sub>4</sub>(OH), G<sub>4</sub>(Br) (Fig. 9-11). The phase behavior of G<sub>1</sub> to G<sub>4</sub> is summarized in Table I (21).

The main difference between these dendrons and the corresponding hyperbranched polymers (18) is that the uniform structures exhibit a second phase which is crystalline at low generations and liquid crystalline at higher generations. This is a common trend which was both theoretically predicted (7) and experimentally observed (3b-e) in the field of macromolecular liquid crystals. Fig. 12 shows the dendrimer obtained from G<sub>n</sub>(OH) and 1,3,5-benzenetricarboxylic acid. The transformation from G<sub>n</sub>(OH) dendron to its "spherical" dendrimeric trimer generates a phase behavior similar to that observed at the transition from G<sub>1</sub>(OH) to G<sub>n</sub>(OH). The complete behavior of these dendrimers will be reported elsewhere (21).

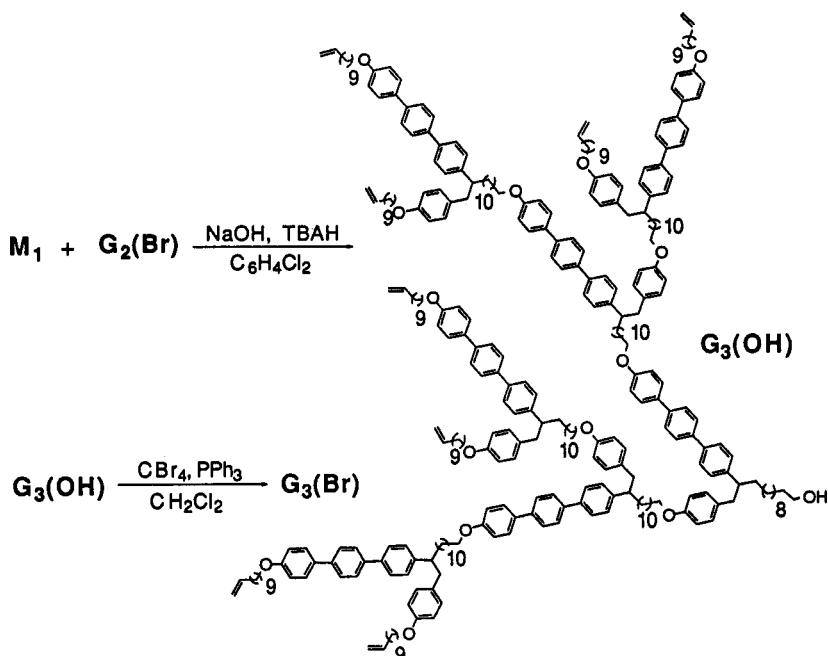
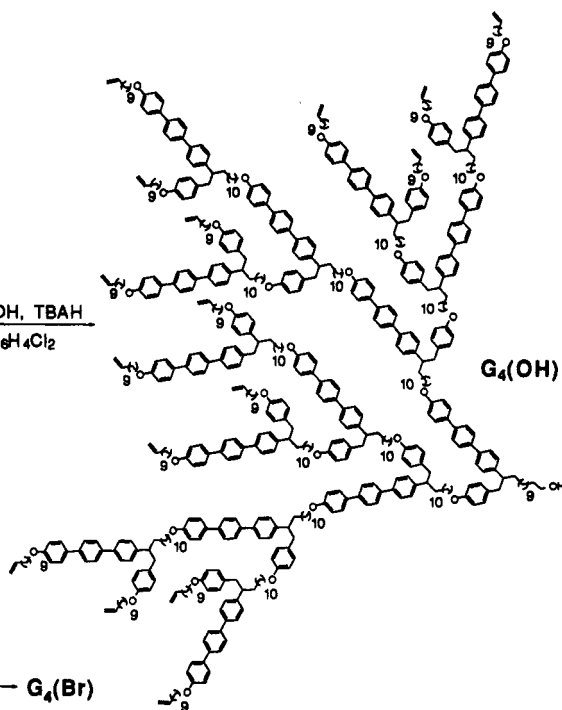
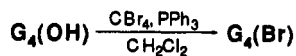
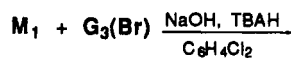


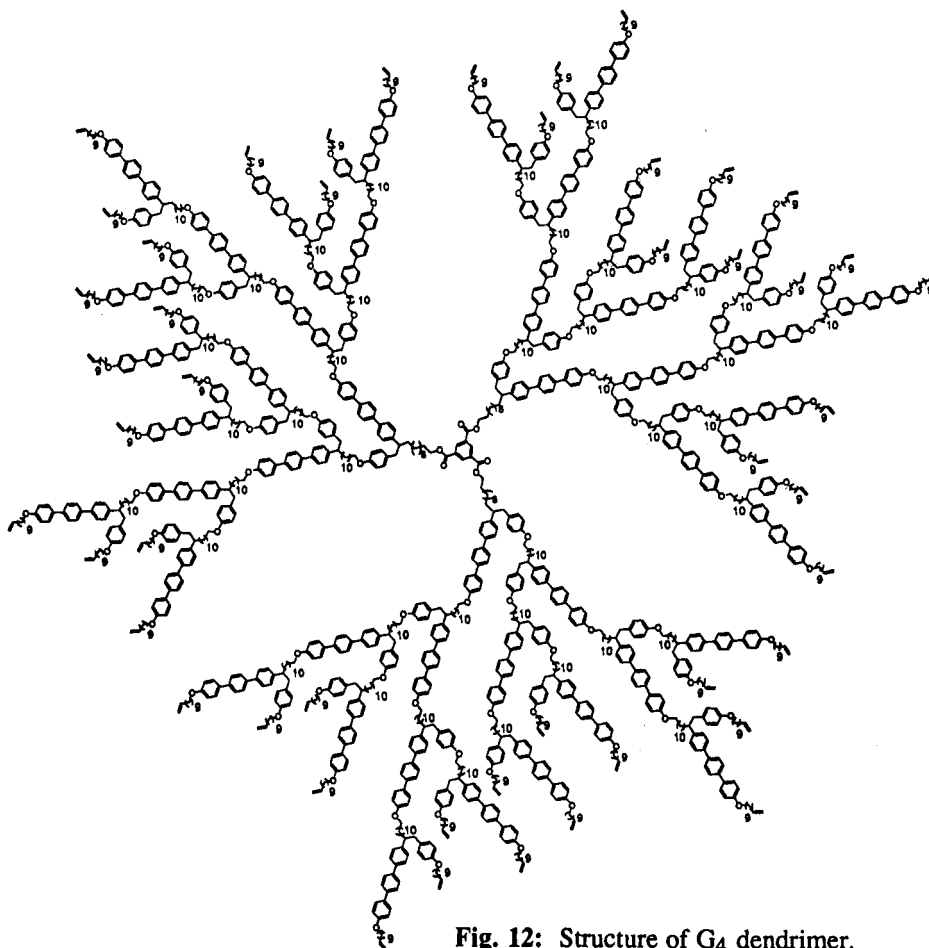
Fig. 10: Synthesis of G<sub>3</sub>(OH) and G<sub>3</sub>(Br).

**Table I: Phase Transitions of G<sub>1</sub> to G<sub>4</sub>**  
(k=crystalline, i=isotropic, n=nematic,  
g=glassy, X=unknown).

G <sub>1</sub> (Br)	k 64 i	i 51 n 40 k
G <sub>2</sub> (OH)	X 62 n 92 i	i 85 n 47 X
G <sub>3</sub> (OH)	X 69 n 105 i	i 98 n 57 X
G <sub>3</sub> (Br)	g 52 X 72 n 104 i	i 97 n 64 X
G <sub>4</sub> (OH)	g 62 X 74 n 110 i	i 103 n 59 X



**Fig. 11: Synthesis of G<sub>4</sub>(OH) and G<sub>4</sub>(Br).**



**Fig. 12: Structure of G<sub>4</sub> dendrimer.**

## Acknowledgments

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## References

1. F. Reinitzer, *Monatsh. Chem.*, **9**, 421 (1988). An English translation is in *Liq. Cryst.*, **5**, 7 (1989).
2. (a) D. Vorländer, *Z. Phys. Chem.*, **105**, 211 (1923); for detailed discussions on the dependence between molecular structure and phase behavior in liquid crystals see: (b) G.W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London, 1962; (c) G.R. Luckhurst and G.W. Gray, *The Molecular Physics of Liquid Crystals*, Academic Press, London, 1979, p. 14; (d) G.W. Gray, *Proc. R. Soc. London, Ser. A*, **402**, 1 (1985); (e) D. Demus, *Mol. Cryst. Liq. Cryst.*, **165**, 45 (1988); (f) D. Demus, *Liq. Cryst.*, **5**, 75 (1989).
3. For some recent reviews on macromolecular and supramolecular liquid crystals see: (a) V. Percec and C. Pugh, *Molecular Engineering of Predominantly Hydrocarbon Based Liquid Crystalline Polymers*, in *Side Chain Liquid Crystalline Polymers*, C.B. McArdle, Ed., Chapman and Hall, New York, 1989, p. 30-105; (b) V. Percec and D. Tomazos, *Molecular Engineering of Liquid Crystalline Polymers*, in *Comprehensive Polymers Science*, First Suppl., G. Allen, Ed., Pergamon Press, Oxford, 1992, p. 300-383; (c) V. Percec, H. Jonsson and D. Tomazos, *Reactions and Interactions in Liquid Crystalline Media, in Polymerization in Organized Media*, C.M. Paleos, Ed., Gordon and Breach, New York, 1992, p. 1-104; (d) V. Percec and D. Tomazos, *Molecular Engineering of Liquid Crystalline Polymers by Living Cationic Polymerization*, in *Adv. Mater.*, **4**, 548 (1992); (e) V. Percec and G. Johansson, *Molecular, Macromolecular and Supramolecular Liquid Crystals Containing Macrocyclic Ligands*, in *Macromolecular Design of Polymeric Materials*, K. Hatada, T. Katayama and D. Vogl, Eds., Dekker, New York, in press.
4. (a) V. Percec and B. Hahn, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 2367 (1989); (b) R.D.C. Richards, W.D. Hawthorne, J.S. Hill, M.S. White, D. Lacey, J.A. Semlyen, G.W. Gray and T.C. Kendrick, *J. Chem. Soc., Chem. Commun.*, 95 (1990).
5. (a) for a review on highly stable lipid membranes from archaeobacterial extremophiles see: K. Yamauchi and M. Kinoshita, *Prog. Polym. Sci.*, **18**, 763 (1993); (b) F. M. Menger, X.Y. Chen, S. Brocchini, H.P. Hopkins and D. Hamilton, *J. Am. Chem. Soc.*, **115**, 6600 (1993); (c) F.M. Menger, S. Brocchini and X.Y. Cheng, *Angew. Chem. Int. Ed. Engl.*, **31**, 1492 (1992); (d) M. Ladika, T.E. Tisk, W.W. Wu and D. Jons, *J. Am. Chem. Soc.*, **116**, 12093 (1994).
6. V. Percec, M. Kawasumi, P.L. Rinaldi and V.E. Litman, *Macromolecules*, **25**, 3851 (1992).
7. (a) V. Percec and A. Keller, *Macromolecules*, **23**, 4347 (1990); (b) A. Keller, G. Ungar and V. Percec, *Liquid Crystal Polymers: A Unifying Thermodynamics Based Scheme*, in *Advances in Liquid Crystalline Polymers*, R.A. Weiss and C.K. Ober, Eds., ACS Symposium Series 435, Washington, DC, 1990, p. 308.
8. V. Percec and M. Kawasumi, *Macromolecules*, **24**, 3618 (1991).
9. (a) V. Percec and M. Kawasumi, *Mol. Cryst. Liq. Cryst.*, **238**, 21 (1994); (b) V. Percec and M. Kawasumi, *J. Mater. Chem.*, **3**, 725 (1993); (c) V. Percec and M. Kawasumi, *Adv. Mater.*, **4**, 572 (1992); (d) V. Percec and M. Kawasumi, *Liq. Cryst.*, **13**, 83 (1993); (e) V. Percec and M. Kawasumi, *Chem. Mater.*, **5**, 826 (1993).
10. V. Percec and M. Kawasumi, *Macromolecules*, **26**, 3663 (1993).
11. V. Percec and M. Kawasumi, *J. Chem. Soc. Perkin Trans. 1*, 1319 (1993).
12. V. Percec and M. Kawasumi, *Macromolecules*, **26**, 3917 (1993).
13. J.F. Li, V. Percec and C. Rosenblatt, *Phys. Rev. E.*, **48**, R1 (1993); (b) J.F. Li, V. Percec, C. Rosenblatt and O.D. Lavrentovich, *Europhys. Lett.*, **25**, 199 (1994).
14. J.F. Stoddart et al, *Angew. Chem. Int. Ed. Engl.*, **33**, 1503 (1994).
15. (a) D.A. Tomalia and H.D. Durst, *Top. Curr. Chem.*, **165**, 193 (1993); (b) J.C. Hawker, K.L. Wooley and J.M.J. Fréchet, *Macromol. Symp.*, **77**, 11 (1994); (c) H.Y. Kim, *Adv. Mater.*, **4**, 764 (1992); (d) J. Issberner, R. Moors and F. Vögtle, *Angew. Chem. Int. Ed. Engl.*, **33**, 2413 (1994).
16. V. Percec, C. Cho, C. Pugh and D. Tomazos, *Macromolecules*, **25**, 1164 (1992).
17. V. Percec and M. Kawasumi, *Macromolecules*, **25**, 3843 (1992).
18. V. Percec, P. Chu and M. Kawasumi, *Macromolecules*, **27**, 4441 (1994).
19. Y.H. Kim, *J. Am. Chem. Soc.*, **114**, 4947 (1992).
20. S. Bauer, H. Fischer and H. Ringsdorf, *Angew. Chem. Int. Ed. Engl.*, **32**, 1598 (1993).
21. V. Percec and P. Chu, in preparation.