Methanofullerenes Functionalized with two Different Liquid-Crystalline Dendrimers

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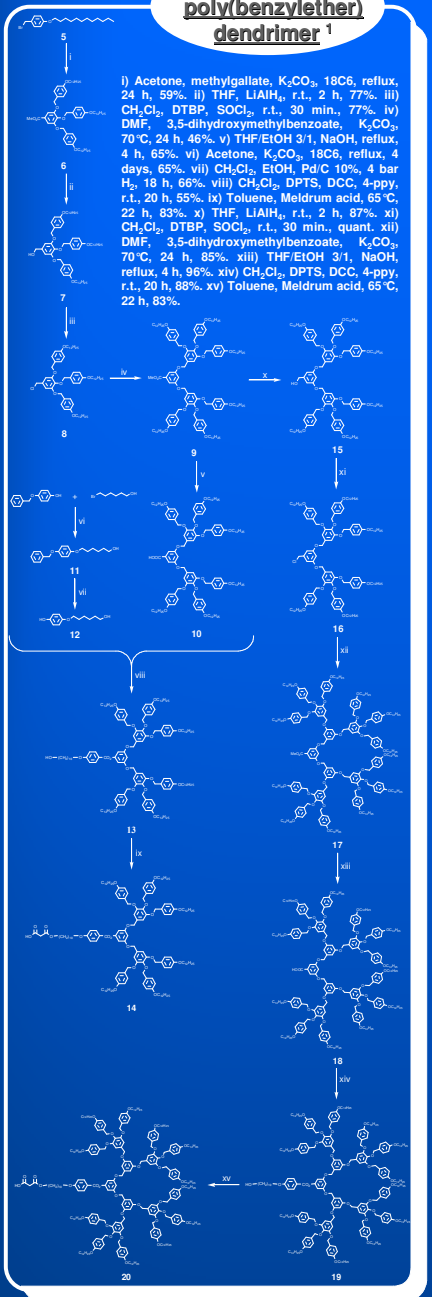
Mesomorphic fullerodendrimers containing poly(benzylether) and poly(arylester) dendrimers of various generations were synthesized in order to study the influence of the dendrimers and [60]fullerene (C_{60}) on the mesomorphic properties.

The choice of those dendrimers was dictated by their different liquid-crystalline properties. The poly(benzylether) dendrons are disc- or cone-like compounds; they form discs or spheres, which arrange into columnar or cubic phases. The poly(arylester) dendrimers organize into smectic A or nematic phases.

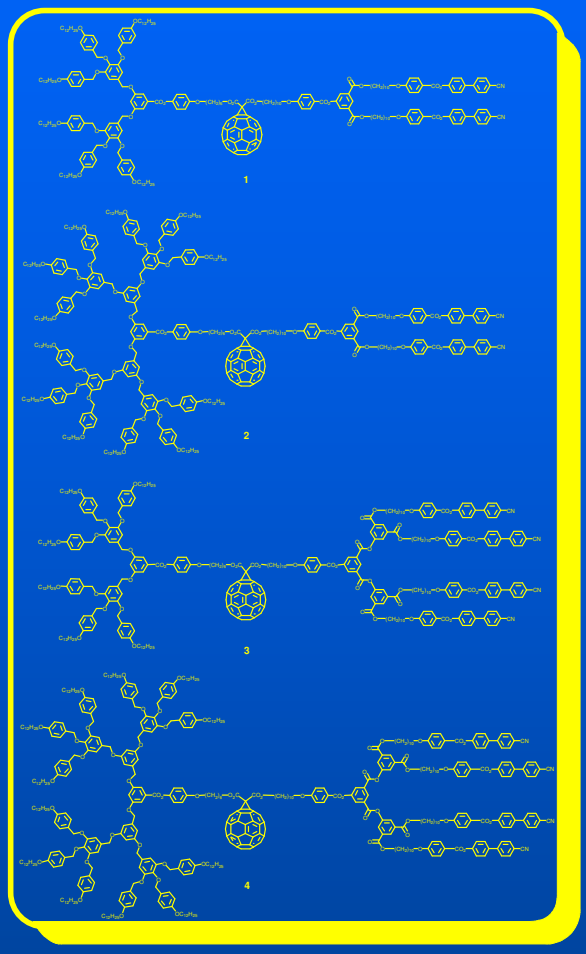
The four possible combinations from the second and third generation of (4-3,4,5-(3,5)n-1)12Gn poly(benzylether) dendrimers and the first and second generation of poly(arylester) dendrimers are presented below.

Synthesis of a poly(benzylether) dendrimer [1]

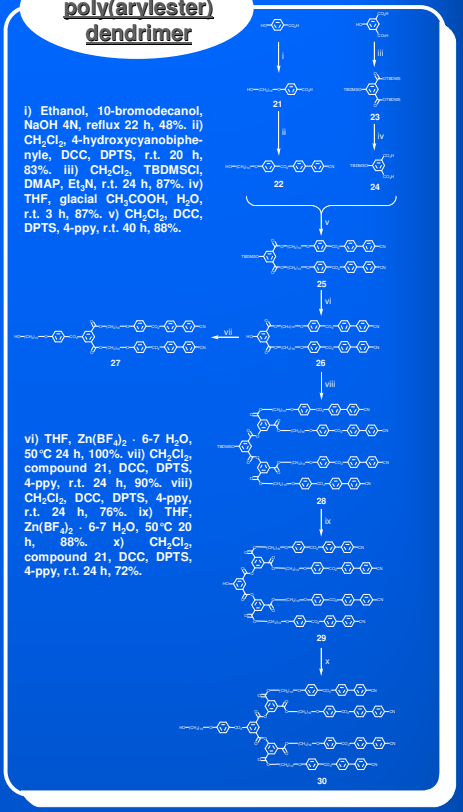


i) Acetone, methylgallate, K_2CO_3, 18C6, reflux, 24 h, 59%. ii) THF, $LiAlH_4$, r.t., 2 h, 77%. iii) CH_2Cl_2, DTBP, $SOCl_2$, r.t., 30 min., 77%. iv) DMF, 3,5-dihydroxymethylbenzoate, K_2CO_3, 70°C, 24 h, 46%. v) THF/EtOH 3/1, NaOH, reflux, 4 h, 65%. vi) Acetone, K_2CO_3, 18C6, reflux, 4 days, 65%. vii) CH_2Cl_2, EtOH, Pd/C 10%, 4 bar H_2, 18 h, 66%. viii) CH_2Cl_2, DPTS, DCC, 4-ppy, r.t., 20 h, 55%. ix) Toluene, Meldrum acid, 65°C, 22 h, 83%. x) THF, $LiAlH_4$, r.t., 2 h, 87%. xi) CH_2Cl_2, DTBP, $SOCl_2$, r.t., 30 min., quant. xii) DMF, 3,5-dihydroxymethylbenzoate, K_2CO_3, 70°C, 24 h, 85%. xiii) THF/EtOH 3/1, NaOH, reflux, 4 h, 96%. xiv) CH_2Cl_2, DPTS, DCC, 4-ppy, r.t., 20 h, 88%. xv) Toluene, Meldrum acid, 65°C, 22 h, 83%.

[1] Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* 2001, *123*, 1302.



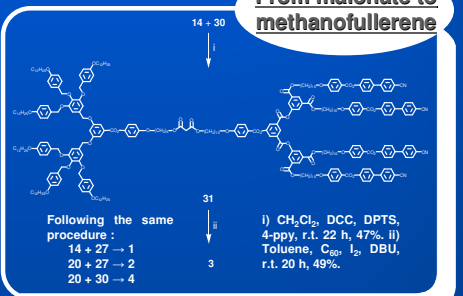
Synthesis of a poly(arylester) dendrimer



i) Ethanol, 10-bromodecanol, NaOH 4N, reflux 22 h, 48%. ii) CH_2Cl_2, 4-hydroxycyanobiphenyle, DCC, DPTS, r.t. 20 h, 83%. iii) CH_2Cl_2, TBDMSCl, DMAP, Et_3N, r.t. 24 h, 87%. iv) THF, glacial CH_3COOH, H_2O, r.t. 3 h, 87%. v) CH_2Cl_2, DCC, DPTS, 4-ppy, r.t. 40 h, 88%.

vi) THF, $Zn(BF_4)_2 \cdot 6\text{-}7\ H_2O$, 50°C 24 h, 100%. vii) CH_2Cl_2, compound 21, DCC, DPTS, 4-ppy, r.t. 24 h, 90%. viii) CH_2Cl_2, DCC, DPTS, 4-ppy, r.t. 24 h, 76%. ix) THF, $Zn(BF_4)_2 \cdot 6\text{-}7\ H_2O$, 50°C 20 h, 88%. x) CH_2Cl_2, compound 21, DCC, DPTS, 4-ppy, r.t. 24 h, 72%.

From malonate to methanofullerene



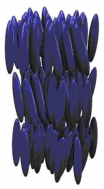
Following the same procedure :
14 + 27 → 1
20 + 27 → 2
20 + 30 → 4

i) CH_2Cl_2, DCC, DPTS, 4-ppy, r.t. 22 h, 47%. ii) Toluene, C_{60}, I_2, DBU, r.t. 20 h, 49%.

Liquid-crystalline phases

Importantly, poly(benzylether) dendrimers display columnar phases whereas poly(arylester) dendrimers display smectic A phases. Combination of both types of dendrimers can give rise to new supramolecular organi-zations.

In columnar phases, disc-like molecules pile on top of each others to form columns. These columns are arranged in a hexagonal or rectangular two-dimensional lattice, and thus give rise to hexagonal (Col_h) or rectangular (Col_r) columnar phases.



In smectic phases, rod-like molecules form layers. In a smectic A phase, the molecules are oriented perpendicularly to the layer planes.

Table 1 : phase transition temperatures and enthalpy changes

Compound	T_g [°C]	Transitions [a]	T [°C]	ΔH [kJ/mol]
1		G → Col_r	75	0,4
		Col_r → I	97	17,7
2		G → Col_r	83	1,4
		Col_r → I	110	18,7
3	45	S_A → I	147	22,2
4	[b]	Col_r → Col_r'	99	3,5
		Col_r' → Col_h	150	6,2
		Col_h → I	157	10,3

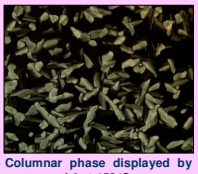
[a] Col_h = columnar hexagonal phase, Col_r, Col_r' = columnar rectangular phases, G = glass state, I = isotropic liquid, S_A = smectic A phase, T_g = glass transition temperature. [b] No detected.

Mesomorphic properties

The mesomorphic and thermal properties of methanofullerenes 1-4 were investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction. The phase transition temperatures and enthalpy changes are reported in Table 1.

Methanofullerenes 1 and 2 display a non-characteristic texture by POM below 97 and 110°C, respectively. According to the DSC, these products present two transitions, at 75 and 97°C, and 83 and 110°C, respectively. By X-ray diffraction, the higher-temperature phases are identified as rectangular columnar phases.

Smectic A phase displayed by compound 3 at 146°C.



Columnar phase displayed by compound 4 at 153°C.

Methanofullerene 3 displays a smectic A phase. This phase was identified by POM from its characteristic texture and confirmed by X-ray diffraction.

According to the observations by POM and DSC, methanofullerene 4 displays a columnar phase between 150 and 157°C. On cooling the sample, two other transitions were detected at 150 and 99°C. By X-ray diffraction, it was possible to characterize the three phases as rectangular and hexagonal columnar phases.

Conclusion

Four new mesomorphic fullerodendrimers were synthesized by coupling a poly(benzylether) dendrimer and a poly(arylester) dendrimer followed by addition onto C_{60}.

All the compounds display liquid-crystalline properties.

When the generation of the poly(benzylether) dendron is higher than the generation of the poly(arylester) dendron (compounds 1, 2 and 4), the nature of the liquid-crystalline phase is dictated by the poly(benzylether) dendrimer and the methanofullerene display columnar phases, wich are typical phases for poly(benzylether).

When the dendrons have the same generation (compound 3), the final product display smectic A phase. In this case, the liquid-crystalline properties are dicted by the poly(arylester) dendrimer.

Acknowledgments

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