[12] a) The central Al atom is surrounded by an icosahedron of 12 further Al atoms: R. Ahlrichs, S. D. Elliott, *Phys. Chem. Chem. Phys.* **1999**, *1*, 12; b) calculated Mulliken charges for Al_{13}^- were $Al_{central} = -1.86$; $Al_{icos} = +0.07$.
[13] For $[Al_7(NH_2)_6]^-$ the Mulliken charge at the central Al atom is -0.18, at the other Al atoms $+0.11$. By contrast, all N atoms are strongly negative (-0.66) and every H atom positively ($+0.20$) polarized. The calculation was carried out in S_6 symmetry with the orientation of NH_2 groups corresponding to that in **1**. The calculated Al–Al lengths are $d(Al2–Al2') = 254.5$ pm and $d(Al1–Al2) = 275.0$ pm. The HOMO-($13a_u$)–LUMO($25e_u$) gap is 1.64 eV.
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[15] The definition chosen by Cotton for a metal cluster[18] is so general that it includes many compounds which bear little resemblance to species such as $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ or the subject of this paper, $[Al_7\{N(SiMe_3)_2\}_6]^-$. By designating these metal-rich molecular species as metalloid clusters, we would like to distinguish them from such compounds. Metalloid (metal-like) clusters should be epitomized by the property that the number of metal–metal contacts exceeds the number of metal–ligand contacts and by the presence of metal atoms which participate exclusively in metal–metal interactions.
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Hyperbranched Polyether Polyols with Liquid Crystalline Properties

Alexander Sunder, Marie-France Quincy, Rolf Mülhaupt, and Holger Frey*

In general, highly branched molecules do not crystallize, but in combination with mesogenic units they can exhibit liquid crystalline (LC) phases.[1] In this context, particularly cascade-branched molecules have been investigated, that is flexible dendrimers[2] and their structurally less perfect analogues, the hyperbranched polymers.[3] In principle, two different strategies have been employed for the incorporation of mesogenic structural elements into cascade-branched architectures (Scheme 1). Either the mesogen can be part of each branching monomer (**a**) or it can be coupled to the end groups of the scaffold (**b**). Structures of type **a** have been prepared by Percec et al. and Ringsdorf et al. for liquid crystal dendrimers as well as hyperbranched polymers.[4] Structures of type **b** with mesogenic end groups attached to flexible dendrimer scaffolds have been the subject of numerous recent publications both of our group as well as others. In almost all cases the formation of smectic phases was observed.[5] To date,

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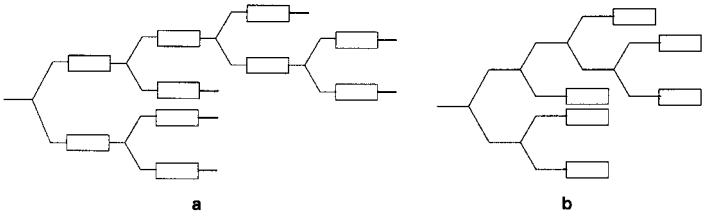

Scheme 1. Structural types of branched LC architectures; rods symbolize rigid structural elements (mesogens); connecting lines indicate flexible parts of the scaffold, for example alkyl chains. **a**: Mesogens are part of every monomer unit of the scaffold, **b**: Structurally isotropic hyperbranched scaffold with mesogenic end groups.

no hyperbranched thermotropic liquid crystal polymers with mesogenic end groups are known, since a fundamental problem is the choice of a suitable flexible and well-defined hyperbranched scaffold.

Recently, we have developed a synthetic strategy based on the ring-opening multibranching polymerization (ROMBP) of glycidol (2,3-epoxy-1-propanol), leading to hyperbranched polyglycerols with narrow polydispersity ($M_w/M_n < 1.5$, mostly < 1.3).[6] By using this approach it was possible to achieve molecular weights of up to 8000 g mol^{-1}, that is 100 hydroxy end groups per molecule. Herein we use these highly flexible aliphatic polyether polyols ($T_g \approx -25\,^\circ$C) to attach mesogenic end groups in order to prepare hyperbranched LC polymers of structural type **b**.[7] We study the effect of molecular weight of the scaffold and the influence of spacer length between mesogen and scaffold on the LC properties.

For the attachment of the mesogenic acids **1** and **2** to the OH end groups of two polyglycerol samples (**PG1**: $M_n = 1500$ g mol^{-1} and **PG2**: $M_n = 3500$ g mol^{-1})[8] we employed a modified esterification with diisopropylcarbodiimide (Scheme 2).[9] In order to obtain a high degree of functionalization of the polyglycerols with mesogens despite the strong difference in polarity between substrate and product, it was necessary to change the solvent in the course of the reaction. However, even after reaction times of several days it was not possible to achieve higher degrees of functionalization than 88 % of all hydroxy groups of the lower molecular weight sample **PG1** (^{1}H NMR, Table 1). For the higher molecular weight sample **PG2** the degree of functionalization ranged between 73 and 79 %. The incomplete reaction of the end groups is most probably explained by the bulkiness of the mesogenic units and the difference in reactivity of the primary and secondary hydroxy groups of polyglycerol.

Gel permeation chromatography (GPC) measurements showed narrow, monomodal molecular weight distributions for all three samples ($M_w/M_n < 1.2$) in agreement with the polydispersities observed for the polyglycerols used (Table 1). The apparent molecular weights determined from GPC (PS standards) correspond to the values calculated from NMR spectra in their order of magnitude.

The LC properties of the three samples prepared were investigated by differential scanning calorimetry (DSC), polarizing microscopy, and wide-angle X-ray scattering (WAXS). In general, all polyglycerols functionalized with mesogenic end groups showed similar phase behavior. In comparison with the unmodified polyglycerol samples, a

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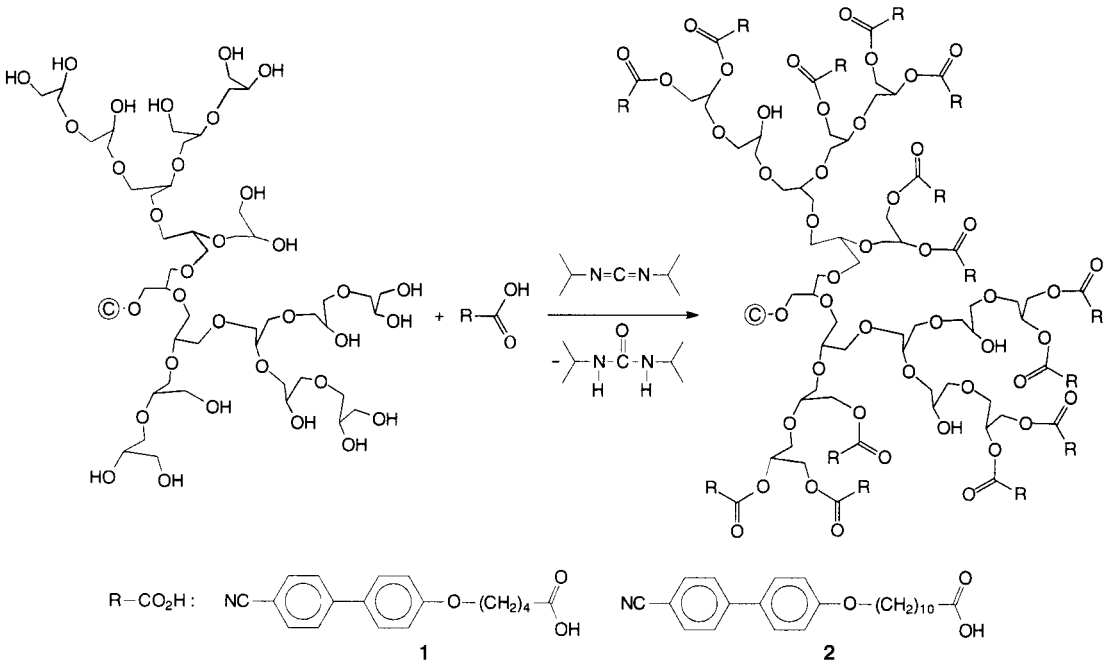
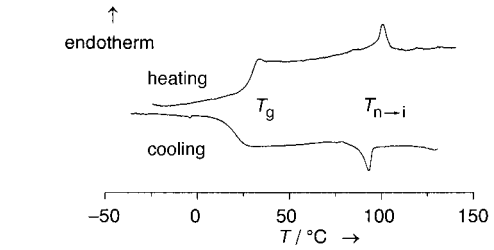


Scheme 2. Functionalization of the end groups of the hyperbranched polyglycerol with mesogenic acids **1** (C_5 spacer) and **2** (C_{11}) by coupling with diisopropylcarbodiimide (DIPC). ©–OH indicates the initiator used for the anionic polymerization of glycidol (ROMBP), which has been incorporated as focal unit ©.

significant increase of the glass transition temperatures (T_g) was observed in all cases. Above the glass transition broad mesophases were detected (Figure 1). Apparently, molecular weight has only a minor influence on the formation of this mesophase (Table 1, **PG1-1, PG2-1**). For both samples the transition enthalpy $\Delta H_{n\rightarrow i}$ of 2 J g^{-1} [10] and the threaded textures observed in the polarizing microscope (Figure 1) unambiguously indicate the presence of a nematic phase.

The phase behavior of **PG2-2** with a longer alkyl spacer between mesogen and hyperbranched scaffold is remarkably different. On the one hand the increase of the glass transition temperature compared to polyglycerol is smaller, on the other hand the temperature interval of the mesophase is broader than in the case of **PG1-1** and **PG2-1**. The transition enthalpy of about 7 J g^{-1} is significantly elevated for a nematic phase, thus indicating the presence of higher ordered smectic clusters (cybotactic structures). However, the diffraction diagrams of all investigated hyperbranched polyglycerols with mesogenic end groups (**PG1-1** as an example in Figure 2) unambigously prove the presence of a nematic phase.

In conclusion, liquid crystalline hyperbranched polymers with narrow polydispersity, in which the LC phase is induced by mesogenic end groups, have been prepared for the first



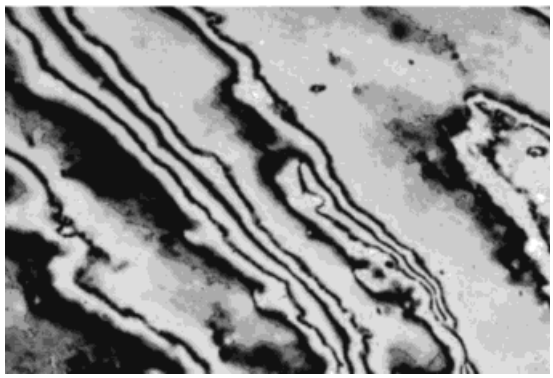


Figure 1. Top: DSC diagram of **PG1-1**. Bottom: Texture of **PG1-1** at 60 °C observed with a polarizing microscope, crossed polarizers.

Table 1. Characterization of the mesogen-functionalized polyglycerols

Sample	M_n[a]	Mes.[b]	f[c] [%]	M_n[d] [g mol^{-1}]	M_w/M_n[d]	T_g[e] [°C]	$T_{n\rightarrow i}$[e] [°C]	$\Delta H_{n\rightarrow i}$[e] [J g^{-1}]	d[f]
PG1-1	1500	**1**	88	5300	1.16	25	97	2.15	4.4
PG2-1	3500	**1**	73	11000	1.13	22	97	2.23	4.4
PG2-2	3500	**2**	79	12800	1.15	15	129	6.77	4.4

[a] Determined by vapor pressure osmometry in methanol. [b] Coupled mesogen: length of spacers **1**: C_5; **2**: C_{11}. [c] Degree of functionalization f determined by NMR spectroscopy: mesogens per OH group. [d] Determined by GPC in $CHCl_3$ with polystyrene standards. [e] Determined by DSC: [f] Layer reflection d determined by WAXS; characteristic for mesogen–mesogen distance.

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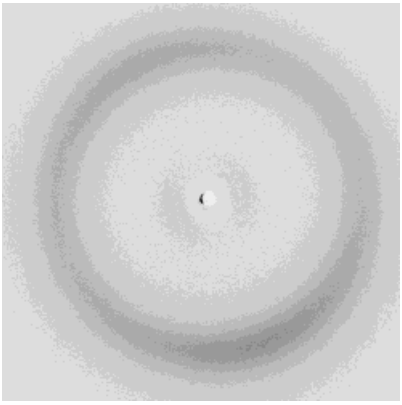

Figure 2. WAXS diagram of **PG1-1**.

time. Interestingly, in pronounced contrast to the structurally related dendrimers with mesogenic end groups[5] broad nematic phases with low viscosities were observed. A complete functionalization of the end groups with mesogens does not seem to be a prerequisite for LC behavior. In comparison with the mesogen-substituted dendrimers, the different behavior may be explained by the spatial distribution of functionalized end groups of the polyglycerols. In contrast to the perfect dendrimer structure the end groups are not located at the same distance from the core. Specific properties of branched molecules, for example, the absence of entanglements and the high concentration of end groups, are promising for the preparation of liquid crystalline materials with low viscosity and possibly short switching times.

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[8] Absolute molecular weights of the hyperbranched polyglycerols were determined by NMR, MALDI-TOF, vapor pressure osmometry.[6] Determination of molecular weights by GPC under standard conditions ($CHCl_3$, PS standards) is not possible.
[9] Exemplified description of the synthesis of **PG2-2: PG2**[6] (0.177 g, 0.51 mmol), acid **2** (1.33 g, 3.51 mmol), and *N*,*N*-dimethylpyridinium *p*-toluenesulfonate (1.06 g, 3.60 mmol) were placed in a 50 mL Schlenk flask and dissolved in anhydrous DMF (13 mL). DIPC (0.6 mL, 3.79 mmol) was added to the clear solution. After the mixture was stirred for five days at room temperature, the solvent was removed and additional acid **2** (0.27 g, 0.71 mmol) suspended in CH_2Cl_2 (15 mL) was added together with DIPC (0.1 mL, 0.63 mmol)(exchange of solvent). After another three days reaction time at room temperature the mixture was twice washed with saturated $NaHCO_3$ solution and water. After removal of the solvent, the organic residue was extracted several times with methanol, dissolved in a little CH_2Cl_2 and precipitated into methanol (crude yield 0.91 g). The crude product was precipitated three times from CH_2Cl_2 into hot ethanol. Yield: 696 mg (61 %) white solid. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 7.7-7.3$ (m, 6H; NCC_6H_4), 6.85 (s, 2H; arom. H), 5.05 (d, 1H; COOCH), 4.35 – 4.0 (d, 1H; $COOCH_2$), 3.85 (s, 2H; $C_6H_4OCH_2$), 3.7 – 3.2 (m, 4H; $COOCCHCH_2OH$, $COOCHCH_2O$), 2.15 (s, 2H; CH_2COO), 1.65 (s, 2H; $C_6H_4OCH_2CH_2$), 1.6 – 1.25 (m, 6H; $OCOCH_2CH_2$, $OCO(CH_2)_6(CH_2)_2$), 1.2 (s, 8H; $OCO(CH_2)_2(CH_2)_4$).
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Ultrastable Mesoporous Aluminosilicates by Grafting Routes**

Robert Mokaya*

There is currently great interest in the thermal and hydrothermal stability of surfactant-templated mesoporous silicas, and recent advances indicate that stable pure silica materials are obtainable.[1–3] However, of greater importance is the stabilization of heteroatom-containing mesoporous silicates which are useful as catalysts or ion exchangers. In particular Al-containing mesoporous molecular sieves which combine stability and enhanced acidity are desireable.[1] Despite the need for such aluminosilicates, there have been very few reports on the stabilization of Al-containing mesoporous

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