Functionalized rod-like polymers: one-dimensional rigid matrices*

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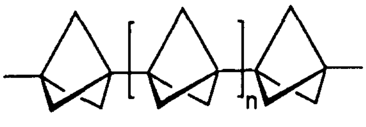
The synthesis of rigid-rod poly([1.1.1]propellane)s and poly(*p*-phenylene)s with hydroxy functionalities in the side chains is described. The suitability of these hydroxy functions as anchor groups for dendritic fragments is investigated. Initial experiments show that not only oligophenylenes as model compounds but also the polypropellane can be dendrimerized to a high degree of conversion. The rigidity of the backbones is considered important in regard to this matter and is therefore addressed theoretically. Molecular modelling calculations based on the AMBER 3.0 force field show that, in fact, the polypropellane backbone is considerably rigid.

(Keywords: poly([1.1.1]propellane)s; poly(*p*-phenylene)s; dendrimers)

INTRODUCTION

An important trend nowadays in organic chemistry is the synthesis of 'extended' molecules, which, owing to their size and often unusual shape, are expected to have interesting properties. The molecular weights of some of these (macro)molecules can already be compared with those of polymers. Towering examples of these are dendrimers, often also referred to as arboroles and cascade molecules. These tree-like structures are of importance as supramolecular functional units, as models for biological functional units and for the field of drug release[1,2]. All dendrimers known today ideally have a spherical shape. Two synthetic strategies are available, namely the divergent[1,3] and convergent[4–6] approaches. Some representatives have already been produced on a technical scale[7].

We are involved in the synthesis of rigid-rod polymers like poly([1.1.1]propellane)s **A**[8] and poly(*p*-phenylene)s **B**[9]. They are obtained as structurally perfect, soluble and processable materials. The key to solubility is the attachment of flexible chains to the monomers. If it were possible to decorate these rods not only with simple alkyl chains but also with chains carrying functional groups, the polymers could then serve as one-dimensional rigid matrices for a variety of fragments. In contrast to flexible polymers, the fragments would have a more or less fixed geometric relation to one another. The attachment of dendritic fragments, for example, would result in a new molecular architecture characterized by a rigid backbone wrapped up by boughs whose branches become increasingly more dense upon going from the inner to the outer regions. The envelope of these polymers would not be a sphere anymore but a cylinder (*Figure 1*). Such macrocylinders, besides their beauty as new supramolecules, may find application in the areas of vesicles and membranes.



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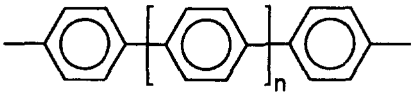

B

The synthetic project outlined above is rather complex and a long-term objective. We present here the first steps along these lines involving (1) the synthesis of poly([1.1.1]propellane)s, poly(*p*-phenylene)s and model compounds with protected functional groups in the side chains, (2) polymer deprotection and (3) the first attempts to attach dendritic fragments of the Fréchet type to the backbones.

EXPERIMENTAL

General

All reagents were purchased from Fluka or Aldrich and used without further purification. The following

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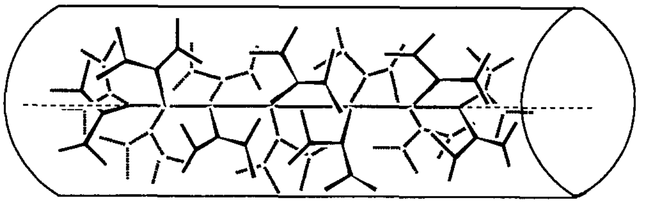


Figure 1 Sketch of a cylindrically shaped dendritic structure derived from a rigid-rod polymer

compounds were prepared according to literature methods: **(G-1)Br**[10], **1a**[11], **1b**[12], **4a**[13], **5**[14,15]and **7a**[13]. The propellanes **1** were used in purities of approximately 98%[11]. The monomers **4a** and **5a** were purified up to 98–99% by column chromatography using deactivated (1–3% H_2O) silica. All solvents were dried under standard conditions. All reactions were carried out under nitrogen and solvents were degassed. ^{1}H and ^{13}C n.m.r. spectra were obtained on a Bruker 270 spectrometer (500 MHz). Size exclusion chromatography (s.e.c.) measurements were carried out using a Waters ultrastyragel linear column (r.i. and u.v. (230 nm) detection; polystyrene standard; THF eluent).

*Poly{[2,2'-methoxy(methyloxymethyl)]biphenylene-4,4'-*alt*-(2,5-dihexyl)phenylene-1,4}* ***6a***

A mixture of **4a** (477 mg, 1.04 mmol), **5** (362 mg, 1.08 mmol) and tetrakis(triphenylphosphine)palladium(0) (36.0 mg, 3 mol%) in 10 ml toluene and 10 ml of a 1 M aqueous solution of Na_2CO_3 was heated to reflux for 48 h. After extraction with ether, the combined organic layers were dried and the solvent removed. The polymer was then dissolved in toluene, precipitated into methanol, centrifuged, recovered and lyophilized with benzene (25 ml). The yield was 360 mg (66%). ^{1}H n.m.r. (ppm) 0.89, 1.24, 1.57, 2.65 (α-CH_2), 3.29 (OCH_3), 4.44 (OCH_2), 4.59 (OCH_2O) and 7.23–7.69 (Ar*H*). ^{13}C n.m.r. ($CDCl_3$) (ppm) 14.09, 22.56, 29.33, 31.60, 32.74, 55.20 (q, OCH_3), 58.46 (t, α-CH_2), 67.56 (t, PhCH_2O), 96.13 (OCH_2O), 128.20, 129.30, 129.60, 131.01, 135.01, 137.57, 138.00, 140.01 and 141.30. Elemental analysis calculated for $(C_{36}H_{48}O_4)_n$: C, 79.38; H, 8.88. Found: C, 79.48; H, 8.63.

*4,4''''-Dibromo-2'',5''-dihexyl-2,2',2''',2''''-tetrakis-[methoxy(methyloxymethyl)]-*p*-quinquephenyl* ***8a***

A mixture of **4a** (4.92 g, 11 mmol), **5** (0.92 g, 2.75 mmol) and tetrakis(triphenylphosphine)palladium(0) (1.0 mol%) in 40 ml benzene and 20 ml of a 1 M aqueous solution of Na_2CO_3 was heated to reflux for 48 h. The aqueous phase was extracted with chloroform, the combined organic layers were dried and the solvent was removed. Column chromatography using hexane/diethyl ether (9:1) as eluent furnished compound **8a**. The yield was 1.07 g (39%). ^{1}H n.m.r. ($CDCl_3$) (ppm) 0.83, 1.20, 1.55, 2.62 (t, α-CH_2), 3.25, 3.30 (2s, OCH_3), 4.33 (s, OCH_2O), 4.54, 4.58 (2s, ArCH_2O) and 7.1–7.8 (Ar*H*).

Deprotection and dendrimerization of ***8a***

Compound **8a** (600 mg, 0.60 mmol) and 0.5 ml concentrated HCl were refluxed in 10 ml methanol/THF (1:1) for 12 h. After cooling the solvent was removed and the obtained white precipitate was washed with cooled acetic acid ester and chloroform. The yield of **8b** was 414 mg (91%). ^{1}H n.m.r. (DMSO-d_6) (ppm) 0.74, 1.10, 1.40, 2.59 (t, 4H, α-CH_2), 4.23 (br m, 8H, ArCH_2O), 7.09–7.18 (4s, 6H, Ar*H*), 7.28 (d, 2H, Ar*H*), 7.49 (d, 2H, Ar*H*), 7.50 (s, 2H, Ar*H*) and 7.74 (br s, 2H, Ar*H*). ^{13}C n.m.r. (ppm) 13.82 (2t, CH_3), 21.86, 30.74, 31.99 (8t, CH_2), 60.17, 60.58 (4t, ArCH_2OH), 120.82 (2s, aromatic *C*Br), 126.92, 127.99, 128.85, 129.19, 131.14, 135.34, 135.90, 136.92, 139.40, 140.15, 140.56 and 142.90 (28s, aromatic C). The signals at 126.92–131.13 ppm were at least 40 Hz broad. To a mixture of purified **8b** (408 mg, 1.90 mmol) and pure sodium hydride (210 mg, 7.00 mmol) in 25 ml dry dimethylformamide (DMF) was added a solution of **(G-1)Br** (7.60 g, 20.1 mmol) in 25 ml DMF. After stirring for 20 h at room temperature, the mixture was heated to 80°C for another 2 h. The mixture was then hydrolysed, the aqueous layer was extracted with toluene and the combined organic layers were dried and concentrated *in vacuo*. The unreacted **(G-1)Br** was removed by column chromatography through silica gel using toluene as eluent. The conversion of this reaction was determined by ^{1}H n.m.r. integration to be virtually 100%. The deprotection and dendrimerization for model **7** proceeded completely analogously.

*Poly{methyloxy(methoxyethyl)[1.1.1]propellane-*co*-pentyl[1.1.1]propellane} 3*

A Schlenk tube (Pyrex) was charged with the purified monomers **1a** and **1b** in the required ratio (*Table 2*) on the gram scale by high-vacuum transfer techniques and AIBN (0.4 mol% of the total amount of propellane) was added. No solvent was added. This mixture was irradiated with a high-pressure mercury lamp (300 W) at 0°C for 20 h. The polymer formed was precipitated into methanol, recovered and then lyophilized with benzene. The yield is given in *Table 2*. ^{1}H n.m.r. ($CDCl_3$) (ppm) (all signals were relatively broad and unstructured) 0.75–2.05 (alkyl H), 3.33 (OCH_3), 3.45 (OCH_2) and 4.59 (OCH_2O). ^{13}C n.m.r. (ppm) 14.1, 22.6, 25.1, 25.4, 29.7, 32.3, 41.1 (q, C-1, C-1', C-3, C-3'), 43.8, 44.0, 44.2 (3t, C-4, C-4'; these carbons show signal splitting owing to tacticity phenomena) 48.6, 55.1 (q, OCH_3), 57.3 (C-2), 61.6 (C-2'), 67.9 (OCH_2O) and 96.2 (OCH_2O).

Deprotection and dendrimerization of 3

A solution of copolymer **3** (*Table 2*, entry 3) (50 mg, 0.25 mmol) in 20 ml THF/methanol (1:1) with a few drops of concentrated hydrochloric acid was refluxed for 18 h. The polymer was precipitated into t-butylmethylether, centrifuged, recovered and dissolved in 1–2 ml DMF without intermediate drying. An excess of sodium hydride that had been carefully washed with toluene and **(G-1)Br** (1.0 g, 2.80 mmol) were added and the mixture was stirred for 15 h at room temperature. The resultant polymer was precipitated into methanol, centrifuged, recovered, dissolved in benzene, precipitated into methanol and lyophilized with benzene. The yield was 45 mg (approximately 40%). For the ^{1}H n.m.r. results see *Figure 2*. The n.m.r. spectrum indicates that there is some residual methoxymethyl-protected functionality.

RESULTS AND DISCUSSION

Some general remarks

The two kinds of polymers used in this project, the poly([1.1.1]propellane)s and the poly(*p*-phenylene)s, differ in the mode of synthesis, the availability of the model compounds, the lengths of the backbones and

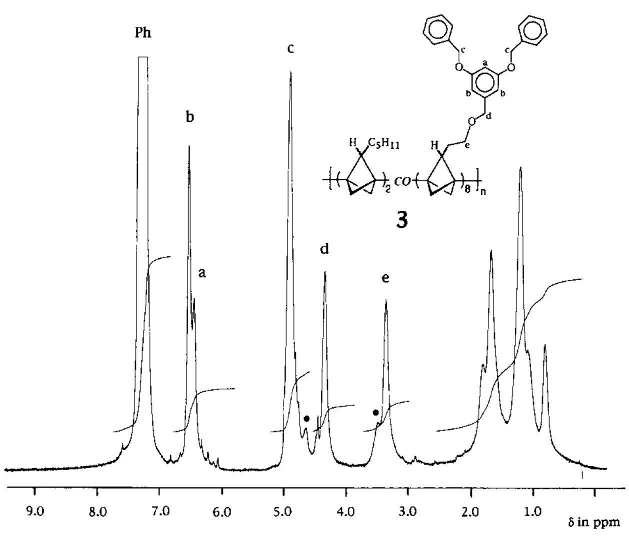


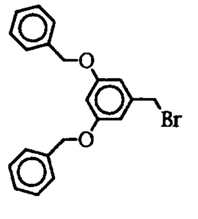
Figure 2 ^{1}H n.m.r. spectrum of copolymer **3** after almost complete dendrimerization with Fréchet-type G-1 fragments. Some residual MOM-protected functionality is marked (●)

Table 1 Comparison of some characteristic features associated with the poly([1.1.1]propellane) **A** and poly(*p*-phenylene) **B** backbones

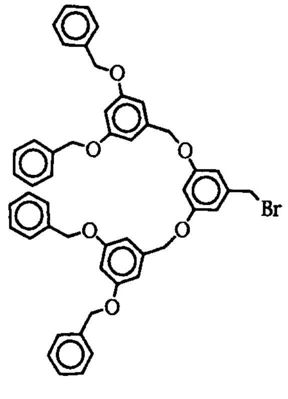
Feature	A	B
Mode of synthesis	Polymerization	Polycondensation
	Radical (or anionic) initiation	Pd catalysed
Degree of polymerization	100–1000	30–90
Polydispersity	Broad; narrow distribution potentially accessible	Broad
Monodisperse rods	Not available	Available through stepwise construction
Model compounds	Practically unavailable	Available in a broad variety
Mode of incorporation of dendritic fragments	Polymer analogous	Polymer analogous or polycondensation of dendritic monomers
Lengths of the rods (Å)	350–3500	125–375
Density of functional groups carrying repeat units	Statistically variable from 0 to 100%	Systematically variable

many other aspects (*Table 1*). They complement each other very well, in fact, and their investigation should result in a conclusive picture of the whole matter.

The main problems are (1) to control the lengths of the rods, (2) to control the dispersity in order to obtain the narrowest possible molecular weight distribution and (3) to achieve a maximum coverage with dendritic fragments. The last of these is inherently associated with the size (generation) of the fragments. There will be an optimum fragment size and distance between the anchor (functional) groups on the backbone. The synthesis of the supramolecules can be approached from two different routes, either by synthesizing a backbone with functional groups to which the dendritic fragments are attached or by subjecting monomers (telomers) that already contain dendritic fragments to a polyreaction. In both cases the rigidity of the backbones should be advantageous because it minimizes difficulties associated with coil formation. In the initial phase of this project we focused on the first approach and used Fréchet-type dendritic fragments of low generation (generations G-1 and G-2)[10]. Since these fragments are obtained by coupling hydroxy functions with benzylic bromides, we limited ourselves to backbones with hydroxy functions.



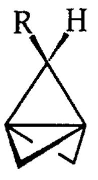
(G-1)Br



(G-2)Br

Backbones with protected functional groups

[1.1.1]Propellanes polymerize with cleavage of the central carbon–carbon σ-bond to give homopolymers with the rigid bicyclo[1.1.1]pentane fragment as the repeat unit[8]. Propellanes with typical functional groups like aldehydes, amines, etc. attached to the hydrocarbon moiety (with or without a spacer) would be ideal. Such substituents, however, cannot be introduced directly because of the reaction conditions which are applied during the synthesis of propellanes (carbene addition, halogen–metal exchange). Recently, the synthesis of the methoxymethyl-protected hydroxyethyl-substituted monomer **1a** was accomplished[11]. The polymerization afforded the high-molecular-weight homopolymer **2a**, which is the first polypropellane to carry substituents that are amenable to further chemical modification[16].



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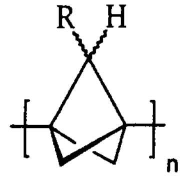


2

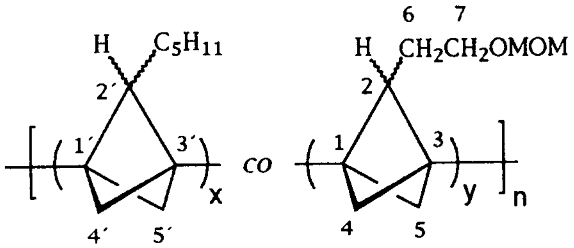
a: R = CH_2CH_2-OMOM
b: R = Pentyl
(MOM = CH_2OCH_3)

We have now additionally prepared a number of copolymers with the general structure of **3** which consist of a random sequence of repeat units with protected anchor groups and solubilizing alkyl chains (*Table 2*). Thus, the density of anchor groups attached to the polypropellane backbone can be varied as required. This

Table 2 Copolymers 3 prepared from monomers **1a** and **1b**

Entry	Feed ratio **1a**:**1b**	Ratio of incorporation **1a**:**1b**	Yield (%)
1	14:86	18:82	56
2	34:66	33:67	60
3	80:20	80:20	57

should (1) help to reduce eventual problems with the solubility of deprotected material and (2) allow the attachment of highly voluminous fragments which could not be attached to the homopolymer. The ratios of incorporation were determined by ^1H n.m.r. integration, comparing the signals of the OCH_2O protons of the methoxymethyl (MOM) group at 4.59 ppm and the methyl protons of the pentyl chain at 0.80 ppm. The incorporation was found to parallel the monomer feed ratio. According to preliminary measurements the molecular weights of the copolymers are of the order $M_{peak} = 40\,000$ (polydispersity, $D = 3$).

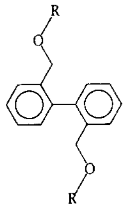


3

Polyarylenes are easily available with a broad variety of substituents through the recently developed Suzuki-type Pd-catalysed polycondensation[9]. Hydroxy-substituted poly(*p*-phenylene)s, however, had not been prepared before now. *Scheme 1* shows how polymer **6a**, a representative of this class, was synthesized starting from the known compounds **4a**[13] and **5**[14,15]. To ensure sufficient solubility during polymer growth and to prevent an eventual detrimental interference of free hydroxy functions with the catalytic cycle, **4b** was converted into its MOM-protected analogue **4a** prior to the coupling. This was achieved by well-known procedures[15]. The purity of both monomers was determined to be greater than 98% by the ^{13}C satellite method, i.e. by comparison of the intensities of the ^{13}C satellites of the MOM methyl group and the α-methylene hydrogens in the ^1H n.m.r. spectra of **4a** and **5**, respectively, with the intensities of the signals caused by impurities. The polymerization was carried out using standard conditions and furnished polymer **6a**. The chemical constitution of **6a** was established by its ^1H and ^{13}C n.m.r. spectra and elemental analysis. The molecular weights were preliminarily determined as $M_n = 20\,000$ and $M_w = 41\,500$ ($D = 2.1$) using s.e.c. in THF.

Model compounds

There is no rational synthesis available for polypropellane oligomers of defined lengths[17]. To avoid rather tedious separation procedures, we therefore decided to do all the work with model compounds and poly(*p*-phenylene) oligomers. They can, in principle, be made as monodisperse compounds by standard coupling procedures[14]. For the present study compounds **7** and **8** were prepared according to a literature method[13] and by coupling an excess of **4a** with **5**, respectively, followed by treatment with acid (see the Experimental section). Longer models are in preparation.



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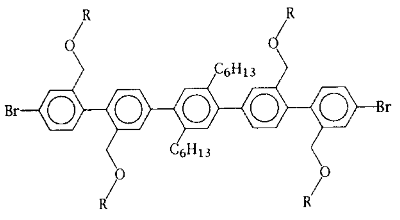
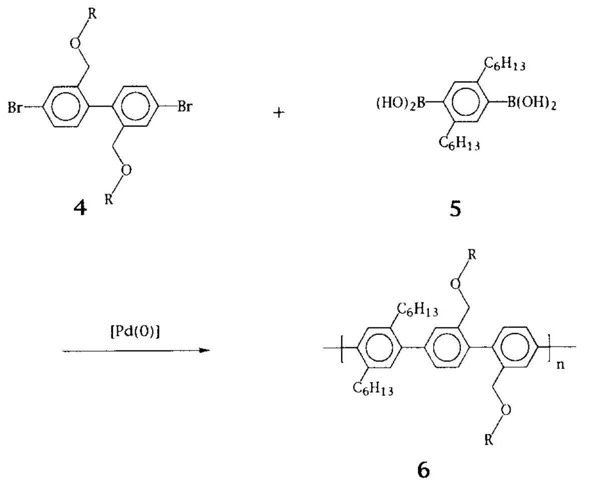


8

a: R = MOM
b: R = H
c: R = G-1

Deprotection and dendrimerization

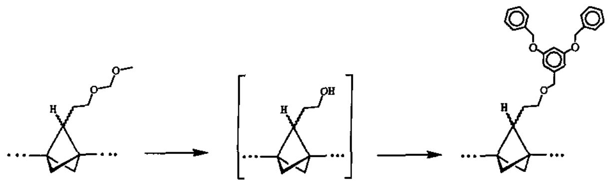
In the initial experiments the compounds **7a** and **8a** were used to determine the conversions of the dendrimerization reactions. Only if very high conversions were observed in these model cases was an analogous polymer dendrimerization feasible. The compounds were deprotected to the corresponding alcohols **7b** and **8b**, respectively, with methanolic hydrochloric acid. The alcohols were then deprotonated with excess sodium hydride. Reaction of the alkoxides obtained with a five-fold excess of **(G-1)Br** gave the dendritic structures **7c** and **8c** in a process which, according to a thorough ^1H n.m.r. analysis (500 MHz), proceeded absolutely cleanly. The conversions reached virtually 100% in both cases. After this promising result, the first polymer dendrimerization was tried using the polypropellane backbone. Unfortunately, the experiments are not yet optimized and fully reproducible, and it is therefore not reasonable to describe them in full detail. The experiments are developed far enough, however, to enable us to prove unambiguously that a polymer dendrimerization of, for example, copolymer **3** with 80% MOM-protected repeat units using the G-1 fragment can be done (see the



6

a: R = MOM
b: R = H
c: R = G-1

Scheme 1 Preparation of poly(*p*-phenylene)s



Scheme 2 Dendrimerization of a polypropellane

Experimental section) (*Scheme 2*). The evidence for the successful reaction stems from an analysis of the ^{1}H (*Figure 2*) and ^{13}C n.m.r. spectra and the solubility behaviour. The n.m.r. spectra show the disappearance of signals for MOM and the appearance of signals for the attached G-1 fragments in the required intensity ratio. The polymer obtained is soluble in THF, toluene, chloroform and other organic solvents. This is in sharp contrast to the deprotected, polyhydroxylated material which cannot be dissolved in these solvents once it has been precipitated and dried. The new polymer also has a very high u.v. absorbance. Additionally, co-injection experiments (s.e.c.) with **(G-1)Br** prove that there is not even a trace of this unreacted compound present. Experiments with other homopolymers, copolymers and larger fragments are under way.

On the rigidity of the poly([1.1.1]propellane) backbone

As mentioned above, we consider the rigidity of the backbones an important factor in the concept of the synthesis of macrocylinders. We therefore did some computer simulations to assess the stiffness of the poly([1.1.1]propellane) backbone and some of the dendritic structures that derive from it. The calculations were based on the AMBER 3.0 force field[18] using a modified version of the AMBER program[19]. The force field was tested by a normal mode analysis of the bicyclo[1.1.1]pentane pentamer. Calculated i.r. frequencies agree well with the experimental data[20]. Some of the peaks, however, could not be reproduced by the force field, mainly because of the absence of coupling terms in the potential functions. Molecular dynamics simulations have been performed with the parent polymer **2** (R = H) and the following dendritic structures derived from polymer **2b**: iso-**2b(G-2)**, iso-**2b(G-3)** and a-**2b(G-3)**, where iso-**2b(G-2)** stands for polymer **2b** with a complete isotactic coverage of fragments of the second generation and a-**2b(G-3)** for the analogous structure with an atactic coverage of third-generation fragments. For **2** (R = H) a chain of 112 repeat units was modelled; for the other systems chains of 10 repeat units were considered. After a thermalization period of 25 ps at 300 K, another 25 ps of simulation time were taken for data collection. A time step of 0.0005 ps was used for all simulations.

The persistence length of a chain molecule can be estimated[21] from the course of the projections of repeat unit vectors j along the chain on a selected reference vector $i \cos \alpha_{ij}$. This was done for the above-mentioned systems, averaged over the time interval of 25 ps. The results are shown in *Figure 3*. Polymer **2** (R = H) has the least decay in persistence, which is clearly a consequence of the fact that all rotatable bonds are co-linear with the chain axis. The persistence length can be given as $\cos \alpha_{ij} = 1/e = 0.368$. This value is presumably not reached for contour lengths less than 200 Å (1 Å = 0.1 nm), which is an indication of considerable rigidity.

The presence of side chains in **2b(G-2)** and **2b(G-3)** obviously influences the behaviour of the backbone. Interactions between side chains tend to distort the backbone. Surprisingly, **2b(G-2)** with its less-extended side chains appears to be less rigid than **2b(G-3)**. The persistence length can be extrapolated to 40–60 Å. This can be explained in terms of side-chain motions resulting from mutual repulsion. The coupling of these motions to the low-frequency vibrations of the backbone results in a certain degree of deformation. For **2b(G-3)**, however, this coupling can no longer deform the backbone to the same extent. The mutual repulsion of the side chains is much more isotropic. Trying to avoid each other, the side chains now attenuate the out-of-axis motions of the backbone. The G-3 fragments thus appear to have a stiffening, rather than deforming, effect on the backbone. There seems to be no influence of tacticity on this phenomenon. Furthermore, it is not very likely that dendrimers with fragments of the fourth and higher generations can be prepared with full occupancy along the backbone.

CONCLUSIONS

This paper provides unequivocal evidence that the convergent dendrimer strategy and the rigid-rod polymer concept can be hybridized, thus creating access to a new class of polymers which, in their final form, should attain the shape of macrocylinders.

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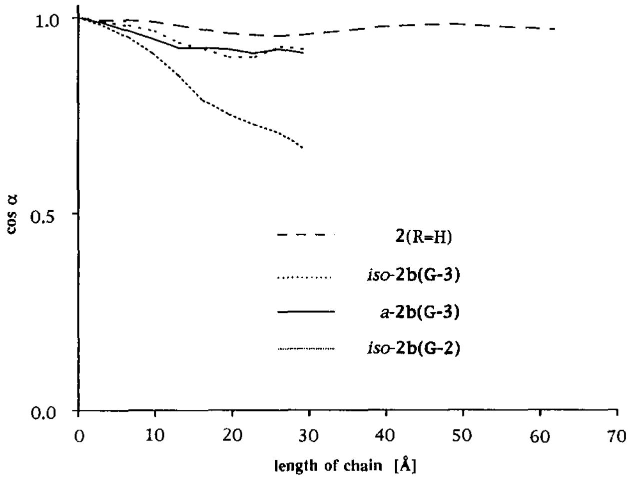

Figure 3 Persistence of the backbones of polymers **2** (R = H), iso-**2b(G-3)**, a-**2b(G-3)** and iso-**2b(G-2)**. The vertical axis shows the cosine of the angle between the first and all following repeat unit vectors. $\cos \alpha = 1/e = 0.368$ corresponds to the persistence length. The values are time averaged from molecular dynamics simulations

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