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Side Chain Dendritic Polymers: Synthesis and Physical Properties

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Abstract: A series of side chain dendritic polymers (SCDP) was produced by copolymerization of dendritic diols of the second, third, and fourth generation with four different semirigid and flexible diisocyanates. The polymerization reactions were conducted both in solution and in bulk. The degree of polymerization and molecular weight distribution of SCDPs were greatly influenced by the flexibility of the diisocyanates and the nature of the reaction medium. The conformation of SCDPs in solution and its dependence on the molecular weight were examined with the aid of intrinsic viscosity ($[\eta]$) measurements. According to the results obtained, SCDPs based on the third and fourth generation monodendrons changed in conformation from spherically to cylindrically shaped structures at a certain molecular weight. The supramolecular assembly of dendritic mono- and polymers in bulk was investigated by X-ray diffraction measurements. It was demonstrated that these macromolecules were, in principle, able to form body-centered cubic lattices. Some results suggested that the ability to form such a type of higher order structures increased as a result of polymerization of dendritic monomers. These findings were supported by molecular dynamics simulations conducted on dendritic mono- and polymers. By means of such calculations, we also studied the effect of the degree of polymerization on the molecular conformation up to a degree of polymerization of seven. We derived the double logarithmic plots of the calculated values of the radius of gyration (R_g) versus molecular weight ($R_g \propto M^{\nu}$). In a medium consisting of a poor solvent, the data scaled according to $\nu = 0.36$, which agreed well with some of the theoretical predictions made for the conventional dendrimers (theory: $\nu = 0.33$). In a good solvent, however, the conformation of SCDPs approached the Gaussian distribution statistics.

Introduction

Mimicking the complex chemical and higher ordered structures, commonly found in nature, constitutes an enormous challenge to contemporary scientists.[1] In biological processes the phenomenon of self-assembly, leading to advanced systems such as micelles and viruses, plays a central role.[2] To mimic these sophisticated structures, a highly versatile synthetic approach is required.[3]

Recently, a new type of macromolecules, termed “dendrimers”, has been synthesized.[4] Dendrimers are monodisperse highly branched regular structures, making them attractive for use as nanoscopic building blocks for ordered supramolecular systems.[5] Owing to synthetic considerations, however, the maximum size of dendrimers is limited[6] and their shape is, in general, restricted to globular and sometimes flat structures. Connecting dendritic macromolecules as the pendant groups to polymeric backbones offers the possibility to create even larger macromolecules. Control of the spatial conformation of the final polymer, and in turn the self-assembly of dendritic groups, may now be possible by altering the structural parameters, such as the degree of polymerization and flexibility of the main chain.

The basic concept of side chain dendritic polymers (SCDP) had been introduced at an earlier stage. Hawker and Fréchet recognized that polymerizing dendritic macromonomers could result in the production of a new class of polymers.[7] The homopolymerization of dendritic macromonomers based on styrene was not possible, which they attributed to the steric congestion at the active centers. The copolymerization of these dendritic monomers with styrene did lead to the formation of a statistical copolymer. Recently, Tomalia and co-workers reported the synthesis of SCDPs by growing the dendritic side groups on the polymer main chain.[8] The authors claim that such a type of architectural polymers was produced by one of them (Tomalia) as early as 1987.[9] However, the unequivocal characterization at that time was not possible owing to inadequate analytical methodology. In addition to these publications, a number of attempts have been made to obtain polymers with pendant dendritic units by the groups of Percec,[10] Schlüter,[11] Ritter,[12] and others.[13] In this regard, the work by Percec and

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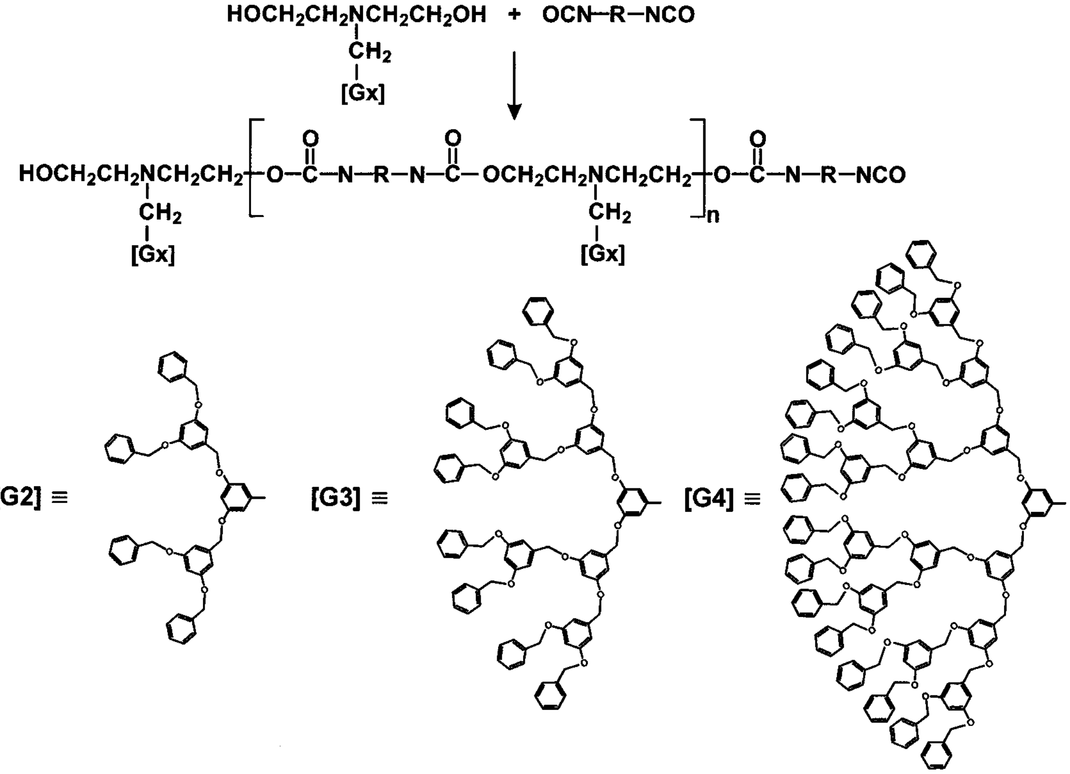
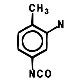
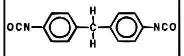
Scheme 1. General Synthetic Scheme Used in the Present Study[a]



[a] See Table 1 for the chemical structure of the diisocyanate compounds.

co-workers should be noted; they used low-generation dendritic units occupied on the periphery by aliphatic chains. According to the authors the self-assembly of flat-tapered and conical monodendrons may produce cylindrical or spherical macromolecules. The subsequent self-organization of these molecules leads to the formation of, respectively, hexagonal and cubic liquid crystalline (LC) phases. The self-assembly mechanism, used by Percec and co-workers, is spontaneous and benefits strongly from the LC behavior of monodendrons which is induced by the alkyl tails. We will show here that the self-assembly of non-LC globular monodendrons may also result in the formation of higher order structures, a which process is reinforced by the polymerization of these macromonomers.

Table 1. A List of Four Different, Commercially Available Diisocyanate Compounds Used in the Present Study

Compound	Structure	Code	Source
1,6-Hexamethylenediisocyanate	$OCN—(CH_2)_6—NCO$	HDI	Aldrich
1,12-Diisocyanatododecane	$OCN—(CH_2)_{12}—NCO$	DID	Aldrich
Tolulene-2,4-diisocyanate		TDI	Fluka
Bisphenol-F diisocyanate		Bis-F	Bayer

The SCDPs reported in the literature are commonly produced by chain polymerization of dendritic macromonomers equipped with functional groups such as styrene or methacrylate. Here, we present a novel synthetic approach based on copolymerization of dendritic diols with various diisocyanates (Scheme 1). We have used Fréchet-type poly(ether) monodendrons which can be easily functionalized with various reactive groups.[14]

The synthetic approach, shown in Scheme 1, is quite versatile and offers many advantages. For example, the molecular structure (conformation) of the resulting polyurethanes (PU) may be regulated by copolymerization of various generations of dendritic diols with different diisocyanates. As can be seen in Table 1, the commercial isocyanate compounds used in this study differ in degree of flexibility and conformation.

In this paper, we will first examine the chemical structure of SCDPs and will discuss the molecular weight values determined by size exclusion chromatography (SEC). The conformation of individual polymer chains in solution, as a function of molecular weight, is studied with the aid of intrinsic viscosity

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measurements. The aggregation of SCDPs, in solution, is investigated by conducting interfacial tension measurements, and in order to establish the self-assembly in bulk, we have applied the X-ray diffraction technique. The experimental results are compared, in a number of instances, with the data obtained from molecular dynamics simulations, and the whole is used to create some fundamental understanding of the physical behavior of SCDPs.

Experimental Section

Materials and Synthesis. All diisocyanates were commercial materials and were used as received. The monodendrons were synthesized by SYNCOM B.V. according to the following general synthetic procedure. A 30 g (9 mmol) sample of chlorine-functionalized monodendrons ([G4]-Cl)[15] was dissolved in 300 mL of acetone. A 18.75 g K_2CO_3 (15 equiv) portion and a 14.1 g diethanolamine (15 equiv) portion were added at once. The mixture was heated under reflux overnight under a nitrogen atmosphere. The mixture was cooled, and the solvent was evaporated. A 200 mL CH_2Cl_2 sample was added, and the organic layer was extracted with water (twice) and brine. The organic layer was dried ($NaSO_4$), and the solvent was evaporated to give 29.5 g of a yellow oil. This oil was purified by column chromatography (SiO_2, eluent CH_2Cl_2 (100%) gradient to CH_2Cl_2/CH_3OH (95/5)) to yield 19.2 g (63%) of dendritic diol [G4]-$CH_2N(C_2H_4OH)_2$. The [G2] and [G3] analogues were prepared in a similar way. The assignment of the ^1H NMR peaks for [G4]-$CH_2N(C_2H_4OH)_2$ is as follows: ^1H NMR ($CDCl_3$) δ (ppm) 1.5−1.9 (s, 2H, OH), 2.55 (t, 4H, CH_2), 3.4 (m, 6H, CH_2), 4.8 (s, 28H, $ArCH_2O$), 4.9 (s, 32H, $PhCH_2O$), 6.4 and 6.5 (m, 42H, ArH), 7.15−7.3 (m, 80H, PhH).

The polymerization reactions were conducted either in solution or in bulk. The general procedure is as follows. For the polymerization in solution, stoichiometric amounts of a certain dendritic diol and diisocyanate were dissolved in a dried organic solvent (see Table 2). After a small amount of dibutyltin acetate (DBTA; Merck) was added, the mixture was stirred under N_2 atmosphere overnight at room temperature. The complete disappearance of all isocyanate groups was checked by FT-IR.[16] The solvent was evaporated under reduced pressure, and the polymeric material was collected.

For polymerization in bulk, the solvent was immediately evaporated under reduced pressure at room temperature upon mixing of two reactive components and the catalyst, i.e., DBTA. The polymerization was conducted in an oven overnight at 60 °C under N_2 atmosphere.

Throughout the text, the polymers are designated according to the code GX-α-β. Here, X is the generation number, α is the abbreviation for the type of diisocyanate (Table 1), and β is the abbreviation for the type of reaction medium, i.e., either solvent or bulk (denoted as B). Various solvents were used: dichloromethane (DCM), tetrahydrofuran (THF), acetonitrile (ACN), chloroform (Chlo), and dioxane (Diox).

NMR Experiments. ^{13}C NMR (100 MHz) and ^1H NMR (400 MHz) spectra were obtained on a Bruker ARX400 400 MHz spectrometer. All measurements were carried out at room temperature using $CDCl_3$ as solvent and locking agent. Chemical shifts were referenced to $CDCl_3$ ($\delta = 76.9$ ppm) or $CDCl_3$ ($\delta = 7.27$ ppm).

Differential Scanning Calorimetry (DSC). The DSC experiments were conducted on a Perkin-Elmer DSC-7 at a rate of 10 °C/min under N_2 atmosphere. The glass transition temperatures are determined from the first cooling run.

Size Exclusion Chromatography (SEC) Experiments. SEC was performed on a Hewlett-Packard chromatograph (HP 1090) equipped with a differential refractometer and differential viscometer detectors placed in parallel (Viscotek 200).

Two sets of SEC columns were applied, viz., two Polymer Laboratories (PL) columns, mixed PL-E, and a set of five columns (Styragel HR 1−5, Waters). The eluent (THF, HPLC grade, Biosolve) was degassed using an Erma ERC-3522 degasser. The solvent flow rate was 1 mL min^{-1}. Measurements were done at room temperature. The molecular weight values were determined on the basis of the principle of universal calibration[17] using polystyrene (PS) standards (PL) having known molecular masses ranging from 0.58 to 2800 kg mol^{-1}. To check the applicability of the universal calibration method for investigated polymers, we compared the results for a few SCDPs with the absolute molecular weight values determined using a light scattering detector (Wyatt Technology DAWN-F DSP) coupled to the SEC equipment. The agreement was quite reasonable. For the SEC measurements, the macromolecules were dissolved in THF at room temperature in a nitrogen atmosphere. The dendrimer solutions were filtered using Millex filters (pore size 0.5 μm). All data were processed using a Compaq (Deskpro XL 450) computer equipped with TRISEC 2.70 software (Viscotek). From the measured intrinsic viscosity [η], as a function of elution volume, the molar mass distribution (MMD) and average molar masses were calculated using the universal calibration. Further Mark−Houwink (M−H) plots (log [η] versus log molar mass) were generated for each of the samples.

Interfacial Surface Measurement. The experiments were conducted according to the drop-volume method[18] using a Lauda tensiometer TVT 1.

X-ray Diffraction Measurements. X-ray diffraction measurements were performed with a powder diffractometer (PW1820) in Bragg Brentano geometry using fixed slits (1° divergency slit; 0.2 mm entrance slit). Cu Kα radiation was used (40 KV, 50 mA), monochromatized with a monochromator in the diffracted beam.

The diffraction patterns were measured under ambient conditions on thin films using sample holders with a Si single-crystal bottom. The mono- and polydendrons were processed on Si plates, starting from a temperature just above the glass transition temperature.

Molecular Modeling Calculations. All molecules have been constructed by means of the builder facility of the InsightII-based MSI package,[19] which was running on a Silicon Graphics Indigo^2 workstation. Force field calculations were performed using Discover95 on an SGI Power Challenge. Three different force fields have been employed, viz., CVFF, CVFFREP, and PCFF. CVFFREP is a modification of CVFF in which only the repulsive van der Waals interactions between the nonbonded atoms are taken into account. This force field has been used as a model for a very good solvent.[20] All structures were first energy minimized until the maximum energy derivative was less than 1.0 kcal/mol•Å. Radii of gyration and diffraction patterns have been calculated by averaging over 500 configurations as obtained from a molecular dynamics (MD) run at room temperature (300 K). For the monodendrons the equilibration time for these MD runs was taken to be 10 ps, whereas the polymeric systems were equilibrated for 25 ps. After equilibration, every 500th configuration was stored. For the polydendrons, reasonable starting structures for the 300 K, simulations were generated by performing simulated annealing runs. The starting temperature was 1500 K, the final temperature 300 K and the temperature step 240 K. The simulation time at each temperature was taken to be 5 ps. In all MD runs the time step was set to 1 fs, the summation method for the nonbonded interactions was set to no cutoff, and a distance-dependent dielectric constant was employed.

Results and Discussion

Chemical Characterization of Side Chain Dendritic Polyurethanes. In Figure 1, the NMR spectra are presented of all three generation dendrimers and the corresponding PUs based on HDI polymerized in bulk. As can be seen, the dendritic side groups remain intact during polymerization at 60 °C. Furthermore, it can be recognized that a series of peaks, between

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[15] Chlorine-functionalized monodendrons of all generations were prepared according to the procedure described by Fréchet and Hawker.[12]

[16] Occasionaly, it was nessecary to continue the polymerization reaction overnight under reflux conditions.

[17] Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B* **1967**, *5*, 753.

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[19] Computational results were obtained using software programs from Molecular Simulations. Dynamics calculations were done with the Discover programs, using the CVFF and PCFF force fields, and graphical displays were printed from the InsightII molecular modeling system.

[20] Scherrenberg, R.; Coussens, B.; van Vliet, P.; Edouard, G.; Brackman, J.; de Brabander, E. *Macromolecules* **1998**, *31*, 456−461.

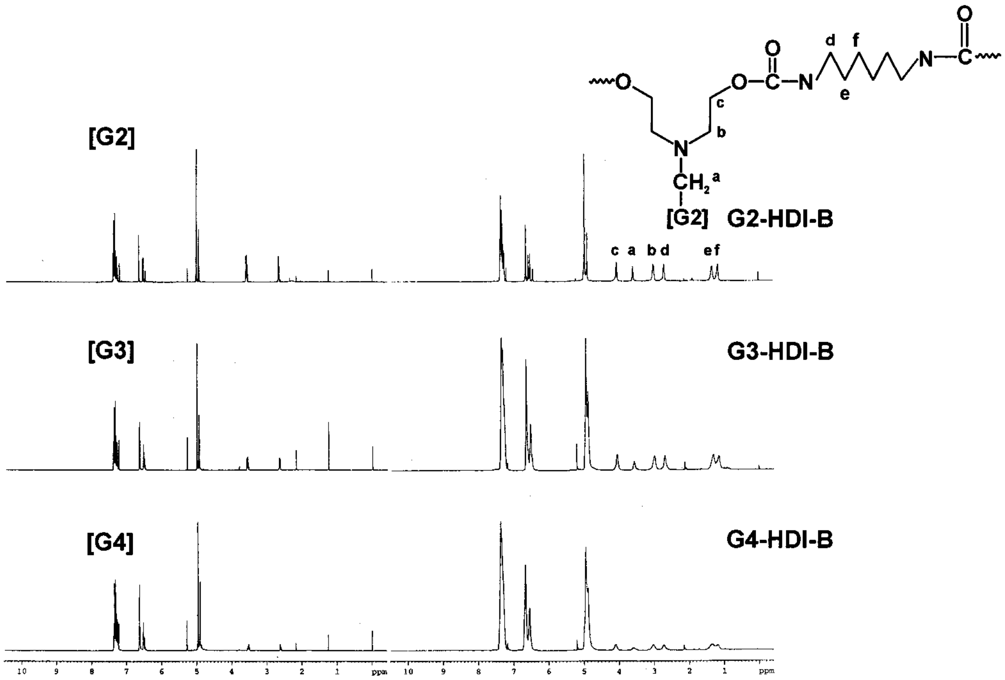

Figure 1. ^{1}H NMR spectra of three SCDPs with different dendritic side groups, G2-HDI-B, G3-HDI-B, and G4-HDI-B. The interpretation of the signals, for the main chain, is given in the inset.

Table 2. Molecular Weight Values of All the Mono- and Polydendrons Determined with the Aid of SEC Using the Universal Calibration[e]

code	M_n[a]	M_w[a]	M_w/M_n	DP[b]	T_g (°C)	conversion[c] (%)
G2-$CH_2N(CH_2CH_2OH)_2$	770[d]	780	1.0		17.8	
G3-$CH_2N(CH_2CH_2OH)_2$	1800[d]	1900	1.0		30.8	
G4-$CH_2N(CH_2CH_2OH)_2$	3300[d]	3300	1.0		37.9	
G2-HDI-DCM	5600	23000	4.0	7	26.2	69.0
G2-DID-DCM	9600	44000	4.5	12	19.8	84.0
G2-TDI-DCM	3600	5600	1.6	4	33.5	86.0
G2-Bis-THF	7000	15000	2.1	8	31.5	99.0
G2-HDI-B	17200	51000	3.0	21	34.3	98.4
G2-DID-B	15700	63000	4.0	19	18.2	98.8
G2-TDI-B	8100	20000	2.4	10	51.2	99.0
G2-Bis-B	15700	126000	8.0	19	45.0	99.9
G3-HDI-DCM	7500	20000	2.7	5	37.3	57.0
G3-DID-DCM	12000	37000	3.1	7	30.8	61.0
G3-TDI-DCM	13000	25000	1.9	8	43.3	96.8
G3-Bis-THF	6700	8700	1.3	4	40.0	88.0
G3-HDI-B	21000	91000	4.2	13	38.5	97.0
G3-DID-B	20000	112000	5.5	12	30.2	97.7
G3-TDI-B	13500	29000	2.1	8	42.4	97.2
G3-Bis-B	27000	83000	3.1	16	44.4	99.0
G4-HDI-DCM	13000	19000	1.5	4	35.9	95.7
G4-DID-DCM	15000	32000	2.1	5	38.0	63.0
G4-TDI-DCM	11000	14000	1.3	3	44.8	67.0
G4-Bis-THF	12500	30000	2.4	4	43.5	59.0
G4-Bis-ACN	16500	26000	1.6	5	38.0	97.2
G4-Bis-Chlo	4200	4200	1.0	1	29.0	19.0
G4-Bis-Diox	5000	5400	1.1	2	36.5	68.0
G4-HDI-B	24000	71000	3.0	7	38.7	92.2
G4-DID-B	31000	90000	3.0	9	35.8	93.5
G4-TDI-B	22000	43000	1.9	7	42.7	95.9
G4-Bis-B	21000	41000	1.9	6	36.5	95.5

[a] Molecular weights are given in g·mol^{-1}. [b] The number average degree of polymerization (DP) is calculated by dividing the M_n values by the theoretical molecular weight values of the monodendrons. [c] These values represent the amount of reacted monodendrons. [d] These are the experimental data. The theoretical values of M_n for G2, G3, and G4 monodendrons are 828, 1680, and 3375, respectively. [e] In the calculations, the concentration of the unreacted monomers is not taken into consideration.

1 and 4.5 ppm, are formed which can be attributed to the urethane bonds connecting the adjacent dendritic groups. The assignment of the peaks, originating from the main chain, is indicated on the spectra. Unfortunately, the nature of the end groups, and consequently the degree of polymerization, cannot be determined on the basis of the NMR experiments. The molecular weight values are calculated with the aid of SEC and are presented in the next section.

Molecular Weight Measurements. In Table 2, the data are presented concerning the molecular weight characterization of all the dendritic polymers. With the aid of the results as presented in Table 2 several interesting trends can be observed.

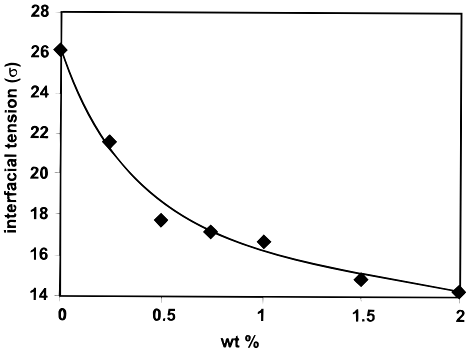

Figure 2. Interfacial tension (σ) measurements of G3-HDI-B in DCM. The leveling off of the drop in σ indicates the initiation of an aggregation process (micellization).

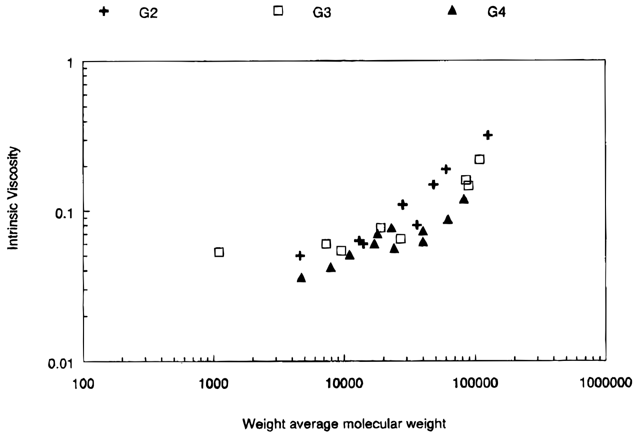

Figure 3. Logarithmic plot of the intrinsic viscosity values ([η]) versus the weight average molecular weight data. Both [η] and M_w values are averaged over the entire molecular weight distribution, inclusive of the monodendrons. The results are presented for all the SCDPs produced with different generations of dendritic groups.

In particular, we will consider the effect of steric hindrance and reaction medium on the course of polymerization. The influence of steric hindrance can be divided into two components: the flexibility of the main chain, i.e., the type of the diisocyanate, and the size of the dendritic groups, i.e., the number of generations.

As can be expected, the number average molecular weight (M_n) or degree of polymerization (DP) for each generation is, generally, the highest for the most flexible diisocyanate, i.e., DID, and the lowest for the most sterically hindered comonomer, i.e., TDI.

In addition to the effect on DP, the flexibility of the diisocyanates seems to have a significant influence on the polydispersity, especially when the polymerization is carried out in solution; M_w/M_n is usually lowest for PUs based on TDI and highest for polymers based on DID. Obviously, the sterically hindered TDI modifies significantly the statistical distribution of the molecular weight; the production of SCDPs with a certain degree of polymerization is favored, and the formation of others is excluded.

When the effect of the monodendron generation on the polymerization is considered, a clear trend can be observed in particular for polymers produced in bulk; both DP and M_w/M_n are lowest for PUs based on G4 and highest for systems based on G2. Here, the strong controlling effect of the size of the dendrimer on the polymerization reaction is unequivocally manifested. Comparison of the polymerization reactions conducted in bulk with those carried out in solution reveals that the degree of polymerization, and conversion of monodendrons, is higher in bulk.

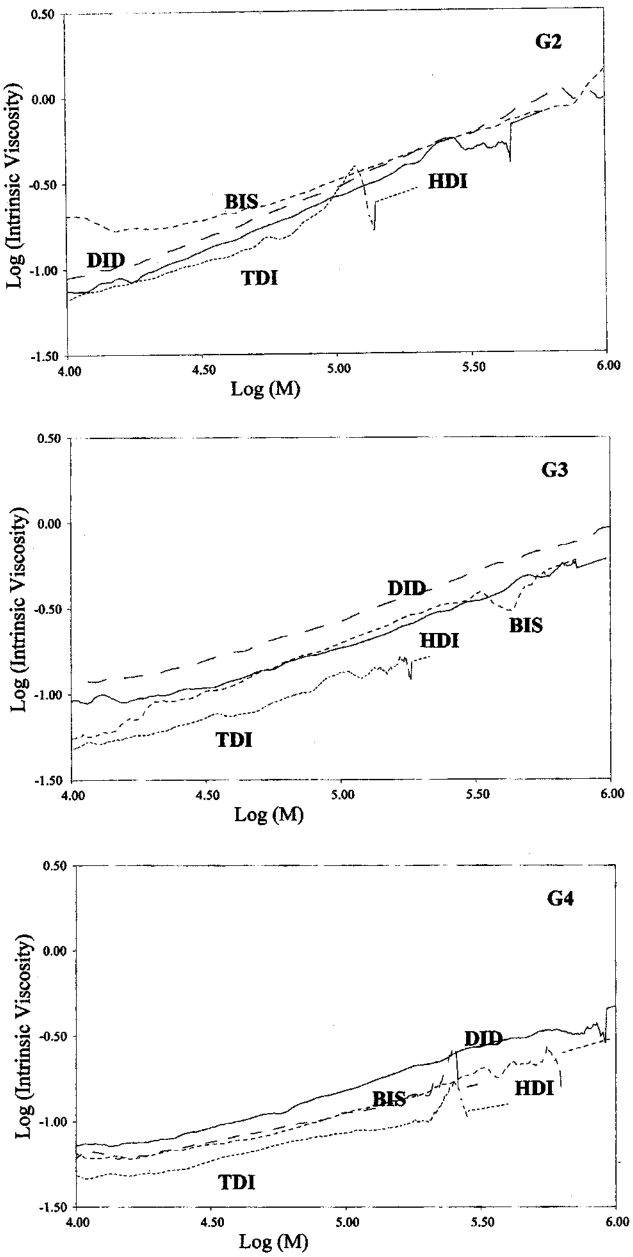

Figure 4. On line intrinsic viscosity ([η]) values for different SCDPs produced in bulk. In each figure, the results are shown for PUs synthesized from identical diisocyanates, but different monodendrons.

The influence of the polarity of the polymerization medium is also investigated for SCDPs synthesized with the aid of the monodendron G4. It is clear that the degree of polymerization is highest for systems polymerized in the most polar solvent, acetonitrile (ACN). In the least polar solvent, chloroform, hardly any reaction has occurred.

The effect of the polymerization medium and the size of the monodendron on the course of the polymerization, i.e., DP and M_w/M_n, can be interpreted in terms of the recent solvatochromic[21] and neutron reflectivity[22] studies on surfactant behavior of comparable Fréchet-type dendritic alcohols. A transition was

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[21] Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1993**, *90*, 4375−4376.

[22] Saville, P. M.; Reynolds, P. A.; White, J. W.; Hawker, C. J.; Fréchet, J. M. J.; Wooley, K. L.; Penfold, J.; Webster, J. R. P. *J. Phys. Chem.* **1995**, *99*, 8283−8289.

Table 3. Slopes Calculated from the Double Logarithmic Plots of [η] versus Molecular Weight for SCDPs Produced in Bulk[a]

	$M = 26\,500$				$M = 145\,000$			
Generation	HDI	DID	TDI	BIS	HDI	DID	TDI	BIS
G2	0.61	0.57	0.46	0.28	0.63	0.71	0.53	0.56
G3	0.31	0.43	0.37	0.35	0.58	0.57	0.47	0.58
G4	0.25	0.37	0.38	0.34	0.40	0.57	0.37	0.36

[a] The slopes are determined in two different regions, i.e., low molecular weight up to 26 500 and high molecular weight up to 145 000.

observed from surfactant to nonsurfactant behavior between the third and fourth generations, which suggests that the alcohol group at the focal point is shielded by the surrounding dendrimer, especially in higher generations. In our case, the shielding of the reactive center by its direct environment is expected to be present during both polymerization in bulk and in solution. In solution, however, the polymerization process may be affected by the possible organization of the mono- and polydendrons in addition to steric hindrance induced by the size of the dendrimer and/or flexibility of the diisocyanates. Judging by the molecular structure of the monodendrons, which consists of a hydrophobic and a hydrophilic part, and on the basis of the results published by Fréchet and co-workers, it is quite possible that dendritic monomers have the ability to form micellar structures in solution. The aggregation number and structure of the micelles would then regulate the accessibility of the functional groups and consequently the maximum degree of polymerization.[23] The upper limit for the number average molecular weight values may be affected when the SCDPs of a certain degree of polymerization start to form micelles. The PUs which have participated in the process of micellization are no longer expected to take part in the polymerization reaction. Evidence for the ability of SCDPs to form micelles is obtained by conducting interfacial tension (σ) measurements between water and dichloromethane.[24] In Figure 2 it can be seen that at a concentration of approximately 0.5 wt % G3-HDI-B in DCM the drop of σ seems to level off, which may indicate that above this critical concentration some type of aggregation process of SCDP has taken place.

Viscosity Measurements. Architectural polymers represent a relatively new class of macromolecules.[25] Where SCDPs are concerned, we are interested in the dependence of the molecular shape and size of dendritic PUs, in very dilute solutions, on the molecular structure. Information about this is obtained by studying the scaling behavior of quantities describing the molecular dimensions, like the radius of gyration (R_g), with the molecular weight of a specific type of SCDP.

Here, we present an analysis of intrinsic viscosity ([η]) data which is a relatively simple and indirect measure of the molecular radius, so-called hydrodynamic volume. [η] can be measured quite accurately using a viscometer detector coupled on line with the SEC equipment.[26]

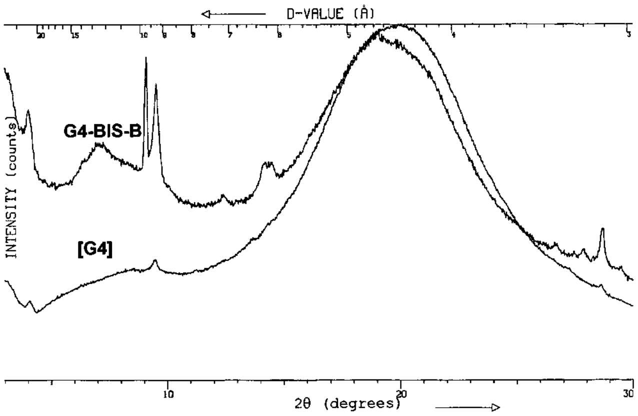

Figure 5. X-ray diffractograms of a thin layer (approximately 1 mm) of two dendritic systems of a [G4] monodendron and [G4]-Bis-B coated on a Si plate.

The viscosity values can be analyzed using the Mark−Houwink equation $[\eta] = KM^a$, where K and a are constants specific for a polymer solvent system. In Figure 3, a plot of the [η] values is presented versus the M_w data on a double logarithmic scale. Commonly, the values of a are associated with the following structures: $a = 0$ (spherical systems), $a = 0.5-0.7$ (random coil flexible chains), and $a = 2$ (rigid rod polymers).[27] As can be seen in Figure 3, there is a drastic change in slope between 10 000 and 60 000, depending on the dendrimer generation. This behavior is not unusual for polymeric systems and has been observed before. Our interpretation of these results is as follows. At low degrees of polymerization, i.e., low molecular weight values, the SCDPs assume a spherical conformation with the PU main chain residing in the core and dendritic side groups acting as the shell. As the degree of polymerization increases the monodendrons do not fit in a globular structure, and as a consequence they force the main chain to assume a more extended conformation. This model is consistent with exponent values of a calculated from Figure 6, $a < 0.3$ (before transition) and $a > 1$ (after transition). For the SCDPs based on [G2] monodendrons, however, the slope is approximately 0.6, indicating that the steric hindrance between the second generation side groups is not sufficient to affect the conformation of the PU main chain significantly. As a result, the structure of these polymers approaches the normal random coil conformation. Similar geometric considerations as above have been used to explain the self-assembly of lipids into, for example, spherical and cylindrical micelles.[28]

Simultaneously with our investigations, both Percec[29] and Tomalia[8] published their results on the same subject. Percec's findings also indicate a transition from spherical to cylindrical SCDPs at high molecular weights. Tomalia showed that the chain extension occurs at G4. As mentioned earlier, for the present system the shape transition takes place at G3 and G4. Even though the chemical structures of the dendritic polymers studied by these authors and us are completely different, the

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(23) Rosen, M. J. *Surfactants and Interfacial Phenomena*; John Wiley & Sons: New York, 1989.

(24) Commonly, the process of micellization in water is studied by conducting surface tension measurements at various concentrations. In our case, however, the dendritic monomers and polymers were not soluble in water. The accuracy of surface tension measurements in organic solvents is quite poor owing to the already low values of the surface tension of pure solvents. Therefore, we were forced to measure the change in interfacial tension between water and some organic solvent, like DCM, at various dendrimer concentrations. These measurements could be carried out with sufficient accuracy. In this connection, we assume that the upper water layer has no significant effect on the process of micellization in the organic medium.

(25) (a) Quirk, P. R.; Zhuo, Q. *Macromolecules* **1997**, *30*, 1531. (b) Heroguez, V., Gnanou, Y., Fontanille, M. *Macromolecules* **1997**, *30*, 4791. (c) Tsukahara, Y., Tsutsumi, K., Okamoto, Y. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 409−413. (d) Tsukahara, Y., Tsutsumi, K., Yamashita, Y., Shimada, S. *Macromolecules* **1990**, *23*, 5201−5208.

(26) a) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401. (b) Mansfield, M. L.; Klushin, L. I. *J. Phys. Chem.* **1992**, *96*, 3994.

(27) Debye, P. J. W. *J. Appl. Phys.* **1944**, *15*, 338.

(28) Israelachivili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1986.

(29) Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S.; *Nature* **1998**, *391*, 161−164.

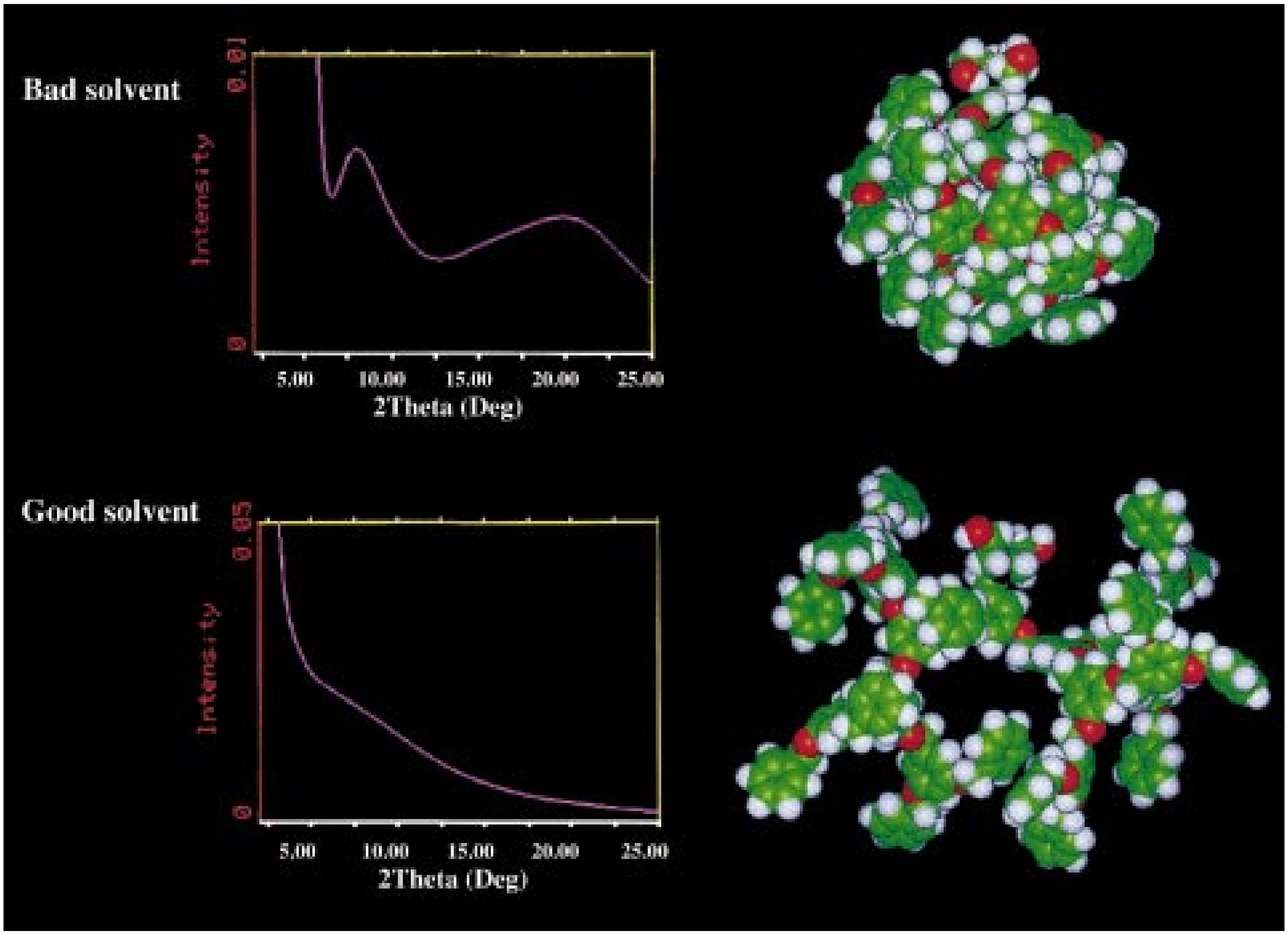

Figure 6. Results of molecular dynamics simulation conducted on a [G4] monodendron, using a poor solvent as well as a good solvent. Both the simulated molecular conformation and the calculated X-ray diffraction based on these structures are displayed.

agreement between the results is quite remarkable. In analogy with SCDPs, cylindrical molecules have also been observed in the case of regular comblike polymers.[30]

The [η] values plotted in Figure 3 are the average data over the whole molecular weight distribution. In addition, no discrimination has been made in this figure between the different types of diisocyanates and polymerization conditions. On line measurements, with the aid of SEC and viscometer equipment, enable [η] to be determined continuously as the polymer solution elutes after the separation step. In Figure 4 the viscosity data are compared for SCDPs with identical PU main chain structures, but with dendritic side groups of different sizes. As can be seen, in analogy with the data in Figure 3, there seems to be a change of the slope at a certain molecular weight. In Table 3 the calculated slope values, for both the low and the high molecular weight regions, are shown.

As can be seen in Table 3, the slope generally decreases; i.e., the polymers become ore denser as the size of the dendritic side groups increases. When SCDPs of the same generation are compared, but based on different diisocyanates, it can be seen that the slope is usually the lowest for SCDPs based on TDI and the highest for those produced from DID or HDI.

X-ray Diffraction Experiments and Molecular Dynamic Simulations. The SCDPs described here do not display any LC behavior. This is concluded from microscopic observation between crossed polarizers in combination with DSC studies which showed, apart from T_g, no other thermal transition. As can be seen in Table 2, T_g is not greatly influenced by the polymerization. As expected, for SCDPs with a given generation of dendrimer, T_g is highest for PUs based on TDI and lowest for those produced from DID.

Even though SCDPs do not show any liquid crystallinity, they seem to be able to form supramolecular structures in bulk. This may be concluded from X-ray diffraction experiments conducted on Si plates coated with the dendritic monomer and polymer. Figure 5 shows the X-ray diffraction pattern of [G4] monodendron and G4-Bis-B. Here, a series of Bragg peaks can be clearly seen, indicating the existence of an ordered structure. On the basis of our calculations, in addition to some small-angle X-ray scattering experiments (not shown here), we concluded that the simplest lattice to describe the structure was cubic with $a = b = c = 20$ Å and $\alpha = \beta = \gamma = 90°$.

Molecular dynamics simulations on [G4] monodendrons, conducted with a poor solvent, show a molecular diameter of 20 Å (see Figure 6a). This suggests that the scattering entity in the cubic crystal lattice is the monodendron. The scattering curve of the entity, i.e., the Fourier transform of the electron density of the molecule, is also given in Figure 6a. The calculated scattering curve corresponds well to the amorphous part of the observed intensities. The good agreement between the calculated and the experimental X-ray diffraction data implies that monodendrons in the condensed phase have the shape of compact spheres. In contrast with the simulation results, shown in Figure 6a, the data obtained from molecular dynamic calculations, conducted in a good solvent, do not correspond at all with the actual results; i.e., both the calculated

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[30] Dziezok, P.; Sheiko, S. S.; Fischer, K.; Schmidt, M.; Möller, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2812.

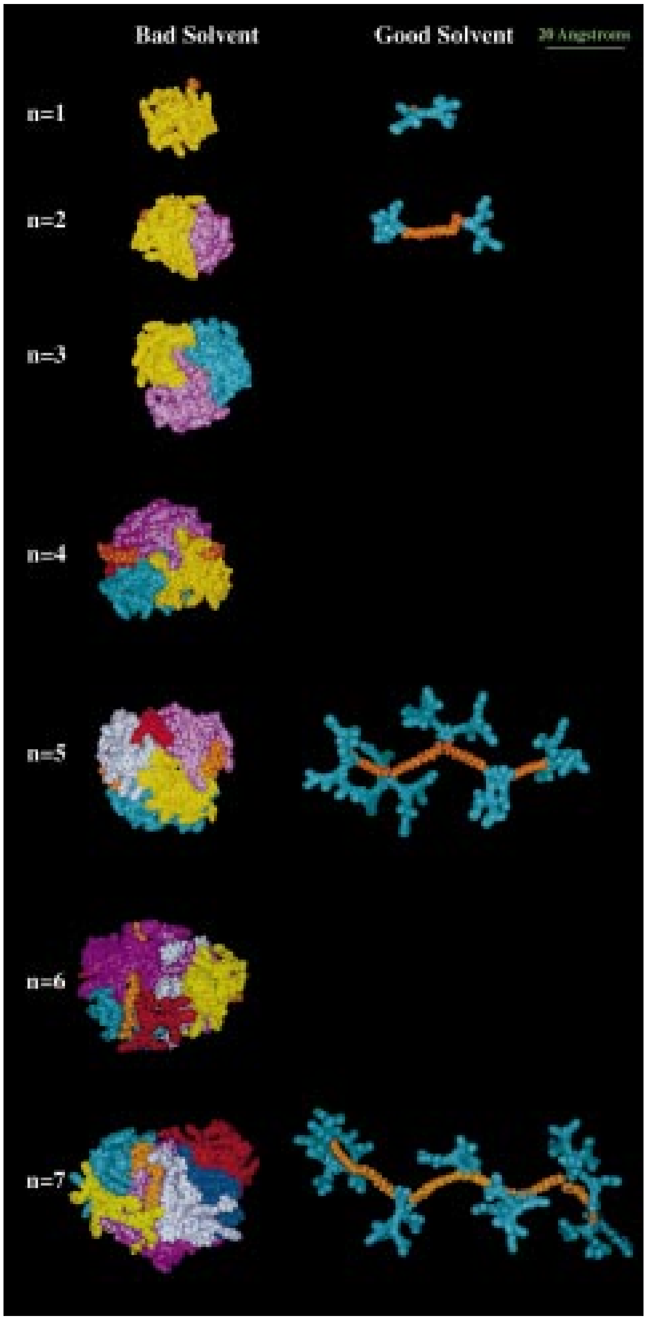

Figure 7. Molecular conformation of [G4]-HDI with different degrees of polymerization (up to 7) calculated with the aid of molecular dynamics simulation with a poor solvent as well as with a good solvent. The calculations under repulsive conditions (good solvent) are limited to the polymerization degrees 1, 2, 5, and 7. To distinguish the various parts, the monodendrons are colored differently in the calculations, simulating the bad solvent.

X-ray diffraction pattern and the molecular radius do not agree with the experimental data[31] (see Figure 6b).

From the molecular dynamics calculations it follows that the volume of the monodendron is 4000 Å^3. As the volume of the unit cell is 8000 Å^3, this leads to the conclusion that the unit cell contains two monodendrons. In the international tables[32] three Bravais cubic lattices are presented: primitive, body-centered, and face-centered. Only with the body-centered cubic (BCC) lattice is it possible to describe the closest packing of spheres with two spheres per unit cell. On the basis of these results, it is concluded that both mono- and polydendrons are able to form a crystalline lattice of the type BCC.

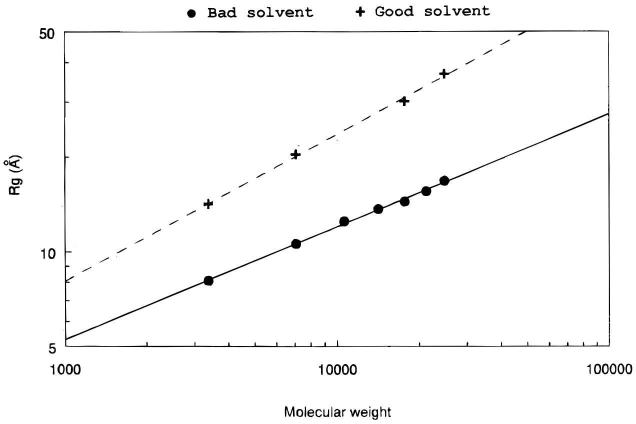

Figure 8. Logarithmic plot of the calculated values of the radius of gyration (R_g), based on molecular dynamics simulation for a poor solvent as well as for a good solvent, versus the molecular weight values. A straight line fit is used with the slope of $\nu = 0.36$ (poor solvent) and $\nu = 0.47$ (good solvent).

Summarizing the above findings it can be said that the spherical [G4] monodendrons have a weak tendency to stack, resulting in the formation of a supramolecular three-dimensional cubic lattice structure. This tendency toward self-assembly seems to increase strongly upon polymerization of these monodendrons.

In Figure 7, the molecular conformation of G4-HDI is displayed for various degrees of polymerization up to seven, calculated with the aid of molecular dynamics simulations in a poor solvent as well as in a good solvent. To distinguish various monodendrons, each is colored differently in this figure. As can be expected, the calculations on the basis of a poor solvent lead to very dense structures, whereas those based on a good solvent result in very open conformations. In Figure 8, the calculated R_g values, extracted from simulation results, are plotted against the molecular weight on a logarithmic scale. As mentioned earlier from the scaling behavior of R_g with molecular weight, valuable information can be deduced regarding the conformation of SCDPs. The calculated sizes of dendrimers, shown in Figure 7, scale with molecular weight, as $R_g \propto M^{n}$ with $\nu = 0.36$ (poor solvent) and $\nu = 0.47$ (good solvent). In the case of random chain polymers in a good solvent, it has been established, both experimentally and theoretically, that $\nu \approx 0.6$.[33] Similar results have been found for star polymers.[34] Obviously, the SCDPs with the side groups of [G4] cannot be considered as flexible Gaussian chains.

Recently there have been several theoretical attempts to analyze the structure of classical dendrimers.[35] These theories provide numerical values for the scaling exponent ν. De Gennes and Hervet, using a self-consistent field analysis, predicted that ν should be between 0.2 and 0.33, depending on the value of a

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(31) The simulated results for molecular dimensions, obtained with a good solvent, were in excellent agreement with the hydrodynamic radii deduced from [η] data. This proves that the eluent for SEC experiments, i.e., THF, can be classified as a good solvent for the monodendrons.

(32) *International Table for Crystallography*; Riedel: Dordrecht, The Netherlands, 1987; Vol. A.

(33) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(34) For theoretical models see: (a) Daoud, M.; Cotton, J. P. *J. Physique* **1982**, *43*, 531−538. (b) Witten, T. A.; Pincus, P. A.; Cates, M. E. *Europhys. Lett.* **1986**, *2*, 137−140. For experimental results see: c) Willner, L.; Jucknischke, O.; Richter, D., Roovers, J.; Zhou, L.-L.; Toporowski, P. M.; Fetters, L. J.; Huang, J. S.; Lin, M. Y.; Hadjichristidis, N. *Macromolecules* **1994**, *27*, 3821−3829. (d) Roovers, J.; Zhou, L.-L.; Toporowski, P. M.; Van der Zwan, M.; Latrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 4324−4331.

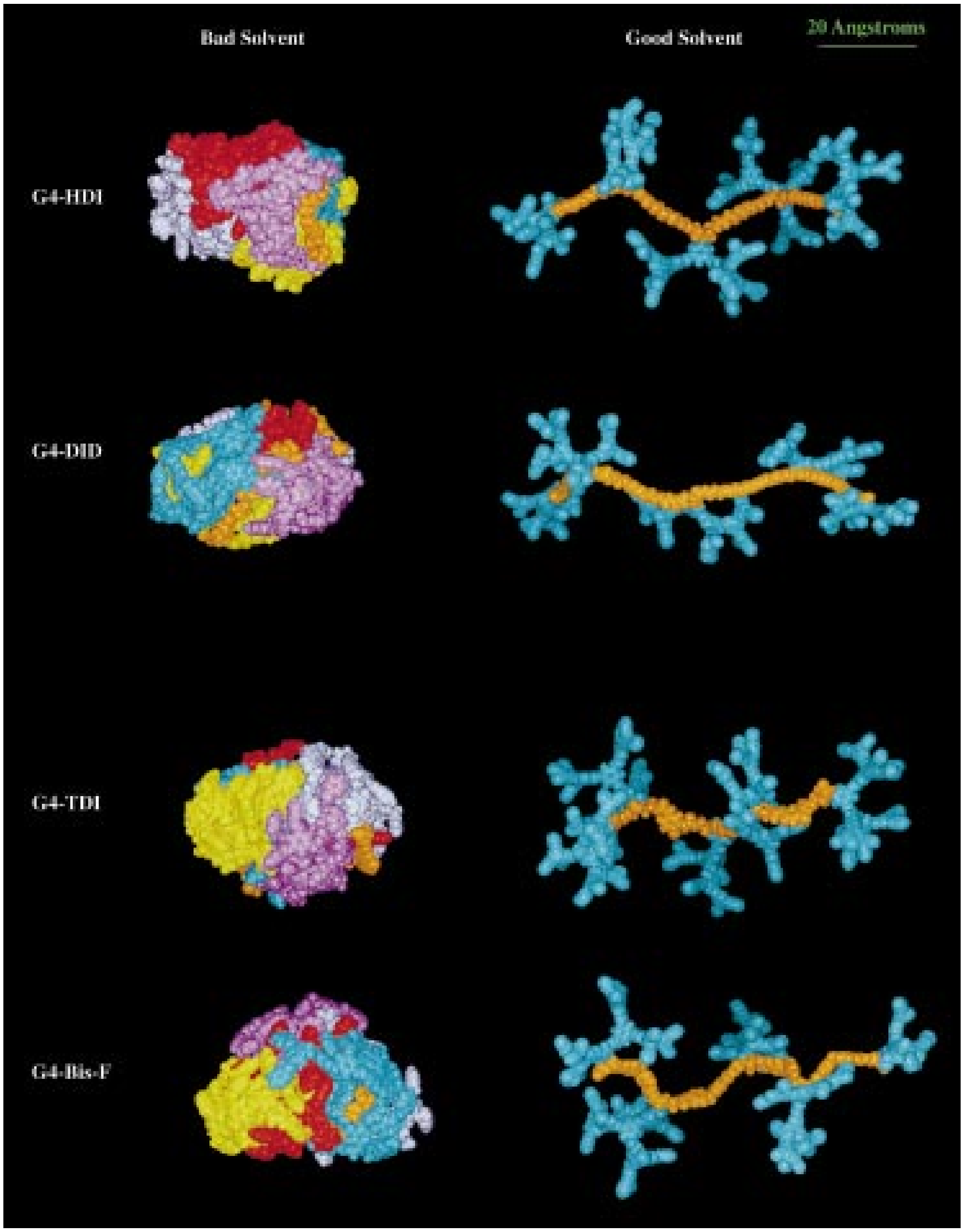

Figure 9. Molecular conformation of a series of SCDPs based on monodendron [G4] produced from different diisocyanates at a fixed degree of polymerization of 5 determined with the aid of molecular dynamics simulation, for a poor solvent as well as for a good solvent. To distinguish the various parts, the monodendrons are colored differently in the calculations, simulating the poor solvent.

certain limiting starburst radius (R_l); this is a radius above which the starburst type of growth cannot exist. Below R_l, ν equals 0.2, whereas above the limiting value, R_g scales with molecular weight according to $\nu = 0.33$. Lescanec and Muthukumar built dendrimers by a kinetic growth algorithm of self-avoiding walks, and according to their simulations $\nu = 0.22 \pm 0.02$. In contrast, Murat and Grest,[36] using molecular dynamics simulations, predicted that R_g should scale with the molecular weight of the dendrimer as $R_g \propto M^{0.33}$, which is in close agreement with our simulation experiments.

From these results it may be deduced that the growth of the size of the SCDPs, based on [G4] in a poor solvent, scales with the molecular weight roughly in a similar manner as the growth of a conventional dendrimer. In a good solvent, however, the growth resembles more the behavior of Gaussian chains.

According to [η] determinations, at a certain degree of polymerization a transition takes place from a spherical to an extended structure for SCDPs of the third and fourth generations (see Figure 3). For PUs based on the third generation dendron, this critical degree of polymerization is equal to approximately 30 units, and for SCDPs consisting of generation four, the transition lies at a weight average molecular weight corresponding to 18 monomers. Therefore, the molecular dynamics simulations have been conducted on the polydendrons in the region before the transition.

With the aid of molecular dynamics simulations, we studied

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(35) (a) de Gennes, P.-G.; Hervet, H. *J. Phys. Lett.* **1983**, *44*, L351. (b) Lescanec, R. L.; Muthakumar, M. *Macromolecules* **1990**, *23*, 2280. (c) Lescanec, R. L.; Muthakumar, M. *Macromolecules* **1991**, *24*, 4892. (d) Mansfield, M. L.; Klushin, L. I. *Macromolecules* **1993**, *26*, 4262. (e) Chen, Z. Y.; Cui, S.-M. *Macromolecules* **1996**, *29*, 7943. (f) Grest, G. S.; Kremer, K.; Witten, T. A. *Macromolecules* **1987**, *20*, 1376.

(36) Murat, M.; Grest, G. S. *Macromolecules* **1996**, *29*, 1278−1285.

the effect of the nature of the main chain, i.e., the type of diisocyanate, on the conformation of SCDPs at a certain degree of polymerization ($n = 5$) in both a good and a poor solvent. The results are presented in Figure 9. As can be seen, the conformations obtained with a poor solvent are globular shaped and rather identical for all diisocyanates. With a good solvent, however, clear differences can be observed between various SCDPs. As can be expected, a PU based on DID adopts the most extended conformation and the SCDP produced from TDI the most compact structure.

Conclusions and Some Final Remarks

We have shown that polyurethanes with pendant dendritic groups of the second, third, and fourth generations can be produced by copolymerization of dendritic diols with various types of diisocyanates. The molecular weight and polydispersity of SCDPs proved to be quite sensitive to the nature of the polymerization medium, i.e., bulk or solution, the flexibility of the diisocyanates, and the generation number of the dendritic monodendrons.

The molecular conformation of the SCDPs in solution was investigated with the aid of intrinsic viscosity measurements. As apparent from the double logarithmic plots of $[\eta]$ versus M_w, a transition takes place from a spherical to a more extended (cylindrical) conformation at a certain degree of polymerization. For polymers with [G2] dendritic side groups, the classical behavior was observed, i.e., the PUs adopt the random Gaussian chain conformation.

The supramolecular self-assembly in bulk was studied by X-ray diffraction experiments. It was shown that the dendritic monomers of the fourth generation are in principle able to form higher-order systems corresponding to body-centered cubic lattice structures. Furthermore, some preliminary results indicate that the ability to form such a type of self-assembled structures is significantly increased as a consequence of polymerization of dendritic monodendrons.

The conformation of several dendritic macromolecules was calculated with the aid of molecular dynamics simulations conducted in a poor solvent and in a good solvent. The logarithmic plots of simulated values of radius of gyration versus molecular weight were also constructed. The growth of the size of a particular type of SCDP, as a function of molecular weight, was in close agreement with the theoretical predictions for classical dendrimers, provided the simulations were carried out in a poor solvent.

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