

Polar and Electrooptical Properties of [60]Fullerene-Containing Poly(benzyl ether) Dendrimers in Solution

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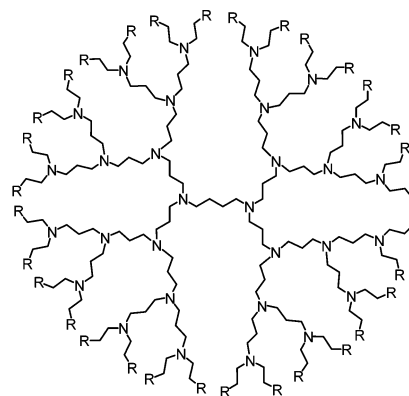
ABSTRACT: [60]Fulleropyrrolidine-containing poly(benzyl ether) dendrimers **1–4** were synthesized via 1,3-dipolar cycloaddition of amino acid and aldehyde derivatives and [60]fullerene. Their dielectric and electrooptical (Kerr effect) solution properties were studied and compared with poly(propyleneimine) dendrimers, namely *DAB-dendr*-(alkyl chain)_n and *DAB-dendr*-(CN)_n, and with known symmetrical and non-symmetrical poly(benzyl ether) dendrimers carrying benzyl groups ([G_x]-[C]-[G_x]) or benzyl and cyanobenzyl groups (CN_n-[G_x]-[C]-[G_{x+1}]), respectively. It was shown that **1–4** display similar polar and electrooptical characteristics independent of their dendrimer generation. This is in contrast to the reference dendrimers for which a strong dependence of total dipole moment on dendrimer generation was observed.

Introduction

Dendrimers are attractive as universal polymer matrices for the construction of materials with desired properties. Their appeal stems from the ability to modify the physical properties of the materials by careful control of the dendritic core, the generation, the end groups, and the length of the spacer between the core and the terminal groups. Such precise control of these structural parameters is possible, due to the varied convergent synthetic methodologies available,^{1–3} and provides access to well-defined materials exhibiting unique properties (monodispersity, low viscosity, thermal stability and good solubility).

There has been growing interest in dendrimers in the fields of surface self-assembly,⁴ optoelectronics,⁵ lithography,⁶ molecular boxes,^{7,8} solar cell devices,⁹ chemical sensors,^{10,11} and drug delivery systems.¹² [60]Fullerene-functionalized dendrimers exhibit fascinating properties, due mainly to the exceptional electrochemical and photophysical attributes of [60]fullerene (C₆₀) and of its derivatives.¹³ Interestingly, in such materials, the dendrimer provides a solubilizing effect (in organic solvents¹⁴ or in water¹⁵) and plays a protecting role¹⁶ (e.g., from solvent molecules or oxygen) for C₆₀. The protective behavior of dendrimers minimizes, and even prevents, the formation of aggregates resulting from C₆₀–C₆₀ interactions, and has led to the elaboration of stable and highly ordered molecular assemblies, i.e., Langmuir and Langmuir–Blodgett films,¹⁷ micelles,¹⁸ membranes,¹⁹ and liquid crystals.²⁰

The electrooptical and hydrodynamic properties of polar liquid-crystalline fullerodendrimers [second-generation poly(aryl esters) functionalized with cyanobiphenyl units] were studied in solution²¹ in order to examine the influence of C₆₀ on the behavior of such sophisticated macromolecules. Those studies demonstrated that C₆₀ (1) had no influence on the hydrodynamic properties (translation diffusion coefficient and intrinsic viscosity value) of the dendrimer, (2) did not significantly disturb the original conformation of the dendrimer (i.e., of the corresponding fullerene-free dendrimer), and (3) only slightly changed the polarity, dielectric polarizability and equilibrium electrooptical properties of the dendrimer. Understanding the influence of C₆₀



DAB-dendr-(CN)_n : R = –CN

DAB-dendr-(alkyl chain)_n : R = –CH₂NH(O)C(CH₂)₁₄CH₃

Figure 1. Structures of poly(propyleneimine) core of fourth generation and terminal groups (other generations are not shown).

could give clues for the design of fullerene-containing materials with tailor-made properties.

We report, herein, the synthesis, characterization, and dielectric and electrooptical (Kerr effect) solution properties of fullerene-containing poly(benzyl ether) dendrimers **1–4** (Chart 1). Their properties were compared with that of two different poly(propyleneimine) dendrimers, i.e., *DAB-dendr*-(alkyl chain)_n and *DAB-dendr*-(CN)_n with *n* = 4, 8, 16, 32, and 64 for the first, second, third, fourth, and fifth generation (Figure 1), and with literature data obtained for symmetrical ([G_x]-[C]-[G_x]) and non-symmetrical (CN_n-[G_x]-[C]-[G_{x+1}]), *n* = 1, 2, 4, 8 and 16) poly(benzyl ether) dendrimers from the first to the fifth generation (Figure 2).²² Despite structural differences between **1–4** and poly(propyleneimine) dendrimers, the latter were selected for comparison purposes as they represent one of the most studied families of dendrimers^{1,2,23,24} and can thus be considered as archetype dendrimers.

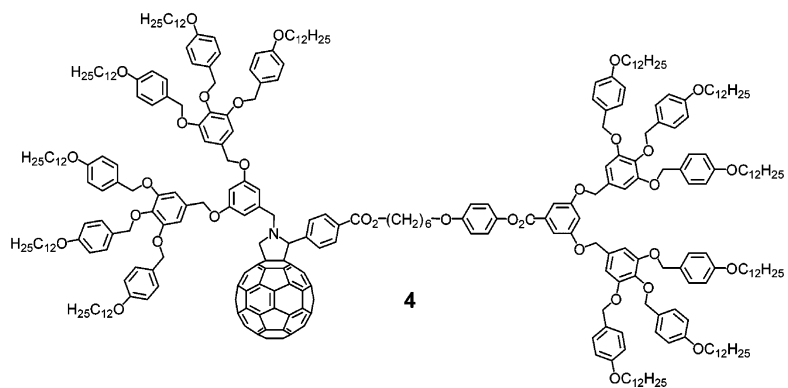
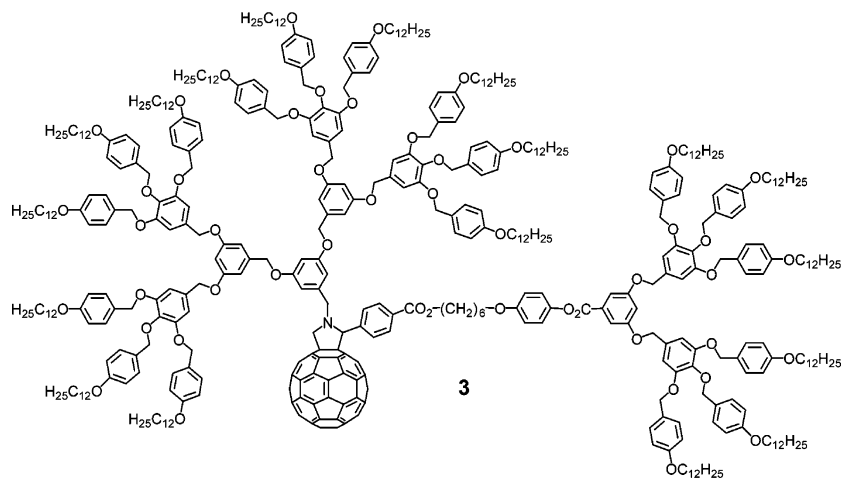
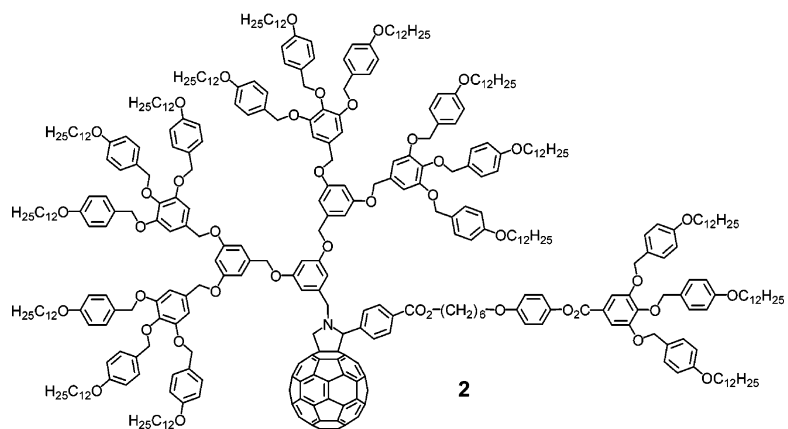
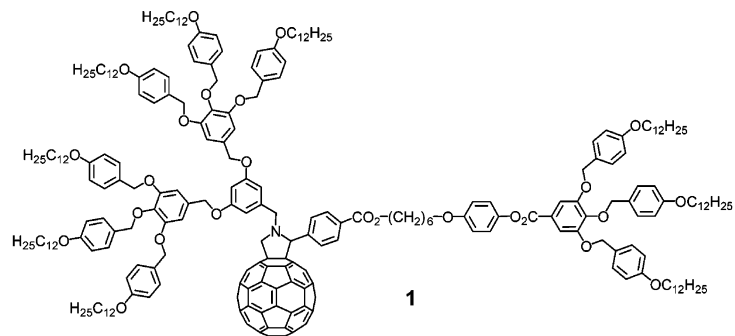
Results and Discussion

Materials. Poly(benzyl ether) dendrimers²⁵ were chosen to functionalize C₆₀ because of their wide use in materials

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Chart 1



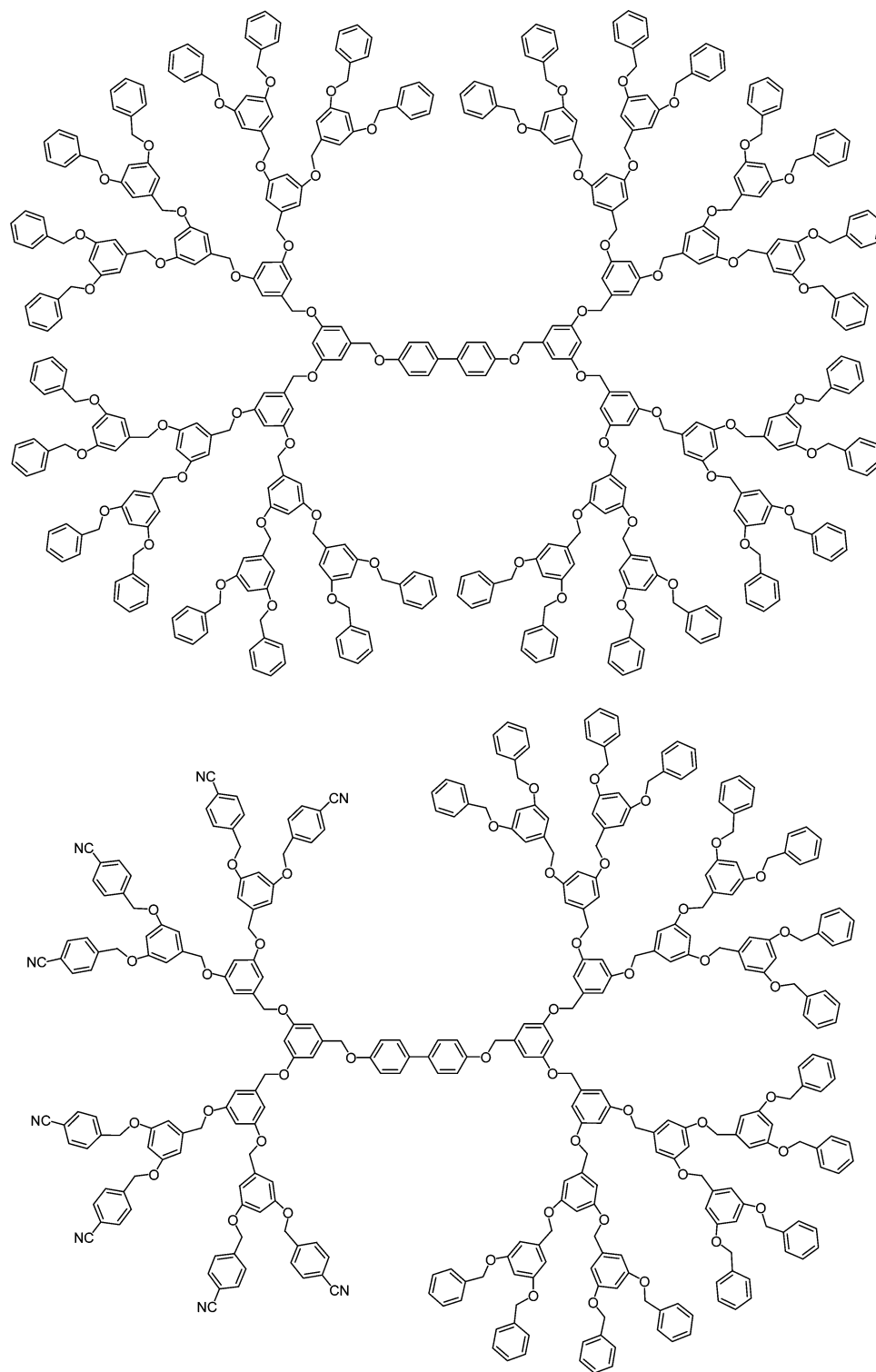


Figure 2. Examples of symmetrical (top) and non-symmetrical (bottom) poly(benzyl ether) dendrimers reported in reference 22. The following abbreviations are used: $[G_4]-[C]-[G_4]$ (top) and $CN_8-[G_3]-[C]-[G_4]$ (bottom).

science.^{26,27} Compounds **1–4** (Chart 1) were synthesized via 1,3-dipolar cycloaddition²⁸ of the corresponding dendritic amino acid and aldehyde derivatives of various generations (see structures in the Supporting Information). This cycloaddition reaction is an elegant and versatile means to assemble two different dendrons, and can therefore be used for the synthesis of codendrimers. Fullero(codendrimers) **1–4** were specifically designed to explore the influence of dendrimer generation on physical properties (**1**, second generation dendrimer and first generation dendrimer; **2**, third generation dendrimer and first generation dendrimer; **3**, third generation dendrimer and second

generation dendrimer; **4**, second generation dendrimer and second generation dendrimer). Compounds **1–4** were isolated as waxy materials; no glass transition could be determined by differential scanning calorimetry. The synthetic procedures and analytical data are reported in the Supporting Information. DAB-dendr-(alkyl chain)_n and DAB-dendr-(CN)_n were synthesized as reported in the literature.²⁴

Experimental Methods and Theory. Permanent dipole moments (μ) were measured by the Guggenheim-Smith method.²⁹ This is derived from the experimental determination of the dielectric permittivity increment $(\epsilon - \epsilon_0)/c$, where $(\epsilon - \epsilon_0)$ is

Table 1. Molecular Mass (M), Fullerene Weight Fraction, Dielectric Permittivity Increment $[(\epsilon - \epsilon_0)/c]$, Squared Refractive Index Increment $[(n^2 - n_0^2)/c]$, Permanent Dipole Moment (μ),^a Specific Dielectric Polarization Values (μ^2/M) and Specific Kerr Constant (K) of 1–4 in Benzene at 21 °C.

compd	M	C_{60} , % wt	$(\epsilon - \epsilon_0)/c$	$(n^2 - n_0^2)/c$	$\mu \times 10^{18}$ CGS units	$(\mu^2/M) \times 10^{36}$ CGS units	$K \times 10^{10}$ CGS units
1	4096.58	17.59	2.11	0.10	8.06	0.016	0.9 ± 0.1
2	6263.74	11.50	1.57	0.11	8.50	0.012	0.7
3	7347.32	9.81	1.35	0.10	8.52	0.010	0.5
4	5180.16	13.91	1.72	0.10	8.14	0.013	0.6

^a 1 D = 10^{-18} CGS units.

Table 2. Molecular Mass (M), Permanent Dipole Moment (μ)^a and Specific Dielectric Polarization Values (μ^2/M) of Symmetrical and Non-symmetrical Poly(benzyl ether) Dendrimers Reported in the Literature;²² the M and μ Values Are Taken from Reference 22.

compd	M	$\mu \times 10^{18}$ CGS units	$(\mu^2/M) \times 10^{36}$ CGS units
CN-[G ₀]-[C]-[G ₁]	604	4.54	0.034
CN ₂ -[G ₁]-[C]-[G ₂]	1266	5.25	0.022
CN ₄ -[G ₂]-[C]-[G ₃]	2589	9.00	0.031
CN ₈ -[G ₃]-[C]-[G ₄]	5236	12.9	0.032
CN ₁₆ -[G ₄]-[C]-[G ₅]	10 530	17.6	0.029
[G ₁]-[C]-[G ₁]	791	2.66	0.009
[G ₂]-[C]-[G ₂]	1640	3.61	0.008
[G ₃]-[C]-[G ₃]	3338	6.14	0.011
[G ₄]-[C]-[G ₄]	6734	7.87	0.009
[G ₅]-[C]-[G ₅]	13 526	12.1	0.011

^a 1 D = 10^{-18} CGS units.

the difference between the dielectric permittivity of the solution and solvent, and on the determination of the squared refractive index increment $(n^2 - n_0^2)/c$, where n and n_0 are the refractive indices of the solution and solvent and c is the solute concentration. The dipole moment (μ) and specific dielectric polarization (μ^2/M) were calculated according to eq 1.³⁰

$$\mu^2/M = 27kT [(\epsilon - \epsilon_0)/c - (n^2 - n_0^2)/c] / [4\pi N_A(\epsilon_0^2 + 2)^2] \quad (1)$$

The μ^2/M ratio characterizes the dielectric polarization of the molecule and is dependent on (1) the permanent dipole orientation in the electric field and (2) the possible induced polarization of the molecule; both factors can contribute to the total ϵ value.²⁹

Dielectric permittivity was measured via a resonance technique at a frequency of 700 kHz using a standard capacity meter E12-1 and a cylindrical titanium capacitor having a capacity of 92.86 pF. The refractive indices (n) were determined using a IRF-23 refractometer at 578 nm (corresponding to the wavelength of Hg).

The optical birefringence of the samples, under a rectangular pulsed electric field (electrooptical Kerr effect), was measured with pulses of 2 ms in a voltage range of 100–1000 V. A compensatory technique with the photoelectric registration of optical birefringence was applied.³¹ A thin mica plate compensator having an optical phase difference of $0.01 \times 2\pi$ was used. A glass cell with titanium semi-cylindrical electrodes with a light path length of 2 cm and a gap between the electrodes of 0.05 cm was used. He–Ne laser (1.5 mW power) with a wavelength of 632.8 nm was used as the light source. Electrooptical properties were characterized by their specific Kerr constant (K) according to relation 2.³²

$$K = \lim_{\substack{E \rightarrow 0 \\ c \rightarrow 0}} (\Delta n/E^2 c) \quad (2)$$

Solution Properties. From the data reported in Table 1, we observe that the total dipole moments (μ) and specific dielectric

polarizations (μ^2/M) of 1–4 are similar despite their structural differences (dendrons of different generations, C_{60} weight fraction). We note that 1–4 possess permanent dipole moments (μ) similar to that of [G₄]-[C]-[G₄] (Table 2).

The concentration dependencies of $(\epsilon - \epsilon_0)$ and $(n^2 - n_0^2)$ for some of the samples are shown in Figures 3 and 4. A linear dependency was observed. From the slopes, the increments $(\epsilon - \epsilon_0)/c$ and $(n^2 - n_0^2)/c$ were determined (Table 1), and used to calculate μ^2/M from eq 1 (Tables 1 and 3). It is important to pay attention to the C_{60} weight fraction as polarization of the fullerene adduct also occurs in an electric field.

Linear dependencies of $(\Delta n_s - \Delta n_o)$ vs E^2 for 1 (in benzene) and DAB-*dendr*-(alkyl chain)₈ (in chloroform) at different concentrations were obtained (Figure 5). The slopes were used to determine $(\Delta n/E^2 c)_{E \rightarrow 0}$. Similar dependencies of $\Delta n = f(E^2)$ (corresponding to Kerr's law) were observed for the other samples. Extrapolation to zero concentration according to relation 2 for 1, 3, and several poly(propyleneimine) dendrimers is presented in Figure 6. No concentration dependence of the specific Kerr constant (K) as a function of concentration was obtained within the concentration range examined.

The fact that the total dipole moment (μ), specific dielectric polarization (μ^2/M) and specific Kerr constant (K) of 1–4 are similar (Table 1 and Figure 7) may be a consequence of the similar symmetries and structural rigidities of 1–4. For DAB-*dendr*-(CN)_n and DAB-*dendr*-(alkyl chain)_n a strong dependence of μ vs dendrimer generation was observed (Table 3 and Figure 7a). This behavior can be explained by the increase in polarity with the generation of the dendritic core. However, the fact that for high generations, DAB-*dendr*-(alkyl chain)_n shows higher μ values than DAB-*dendr*-(CN)_n is an indication that the polar groups located at the periphery of the molecule counterbalance the polarity of the dendritic core due to the orientations of the CN-groups. For the poly(benzyl ether) dendrimers, the total dipole moment (μ) increases with the dendrimer generation (Table 2 and Figure 7a) while the specific dielectric polarization (μ^2/M) is independent of the dendrimer generation (Table 2 and Figure 7b). The different behavior of μ observed between 1 and 4 and the poly(benzyl ether) dendrimers is an indication that C_{60} dictates the shape symmetry of the molecules. It should be pointed out that despite the structural differences, the specific dielectric polarization values (μ^2/M) for DAB-*dendr*-(alkyl chain)_n, poly(benzyl ether) dendrimers and 1–4 are similar within each family, in contrast to the DAB-*dendr*-(CN)_n series (Figure 7b). Those results show that μ^2/M is more strongly influenced by the shape symmetry of the molecules, with little dependence on generation number if the molecules are approximately spherical. This independence of μ^2/M on dendrimer generation was also observed for phosphorus-containing dendrimers.³³ Finally, the similarity in μ^2/M values observed for 1–4 and symmetrical poly(benzyl ether) dendrimers (Figure 7b) strengthens our previous conclusions²¹ that C_{60} has only a small influence on the polarity and dielectric polarization of poly-(benzyl ether) dendrimers.

Table 3. Molecular Mass (M), Permanent Dipole Moment (μ),^a Specific Dielectric Polarization (μ^2/M) and Specific Kerr Constant (K) of DAB-dendr-(CN)_n and DAB-dendr-(alkyl chain)_n of Different Generations in Chloroform at 26 °C.

n^b	DAB-dendr-(CN) _n				DAB-dendr-(alkyl chain) _n			
	M^c	$\mu \times 10^{18}$ CGS units	$(\mu^2/M) \times 10^{36}$ CGS units	$K \times 10^{10}$ CGS units	M^b	$\mu \times 10^{18}$ CGS units	$(\mu^2/M) \times 10^{36}$ CGS units	$K \times 10^{10}$ CGS units
4	300	5.2	0.09	2	1325	4.2	0.013	3.8
8	741			1.5	2789			3.8
16	1622	7.8	0.04		5719	10.0	0.018	3.8
32	3385			1.0	11 578			3.9
64	6910	10.0	0.015	0.5	23 296	14.0	0.009	3.8

^a $1 D = 10^{-18}$ CGS units. ^b Number of peripheral units corresponding to first ($n = 4$), second ($n = 8$), third ($n = 16$), fourth ($n = 32$) and fifth ($n = 64$) generation. ^c From ref 24d.

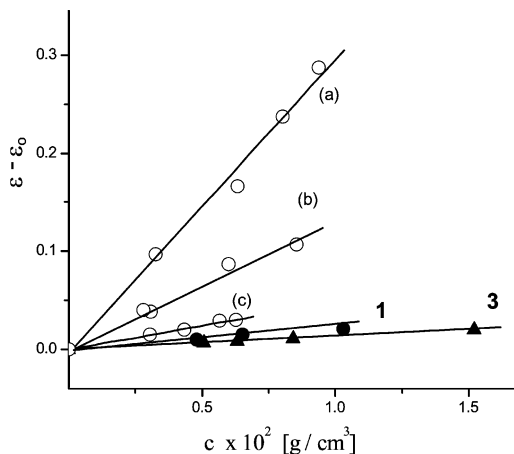


Figure 3. Variation of $(\epsilon - \epsilon_0)$ as a function of the concentration for (a) DAB-dendr-(CN)₄, (b) DAB-dendr-(CN)₁₆, and (c) DAB-dendr-(CN)₆₄ (in chloroform at 26 °C) and for **1** and **3** (in benzene at 21 °C).

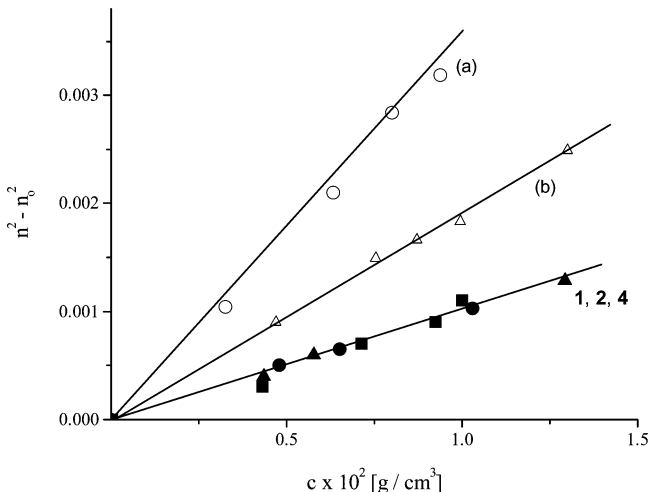


Figure 4. Variation of $(n^2 - n_0^2)$ as a function of the concentration for (a) DAB-dendr-(CN)₄ and (b) DAB-dendr-(alkyl chain)₃₂ (in chloroform at 26 °C) and for **1**, **2** and **4** (in benzene at 21 °C).

The dependence of the specific Kerr constant (K) of **1–4**, DAB-dendr-(CN)_n, and DAB-dendr-(alkyl chain)_n with respect to the generation of the dendritic core is shown in Figure 8. The K parameter depends on polarity, optical anisotropy of polarizability and geometry (see eq 3). For DAB-dendr-(alkyl chain)_n, no variation of K (Figure 8) and μ^2/M (Figure 7b) was observed, whereas for DAB-dendr-(CN)_n a decrease in both K (Figure 8) and μ^2/M (Figure 7b) vs dendrimer generation was obtained. These dependencies can be explained by the fact that DAB-dendr-(CN)_n combines a polar dendritic core with a polar periphery, whereas DAB-dendr-(alkyl chain)_n combines a polar dendritic core with a nonpolar periphery. The results presented

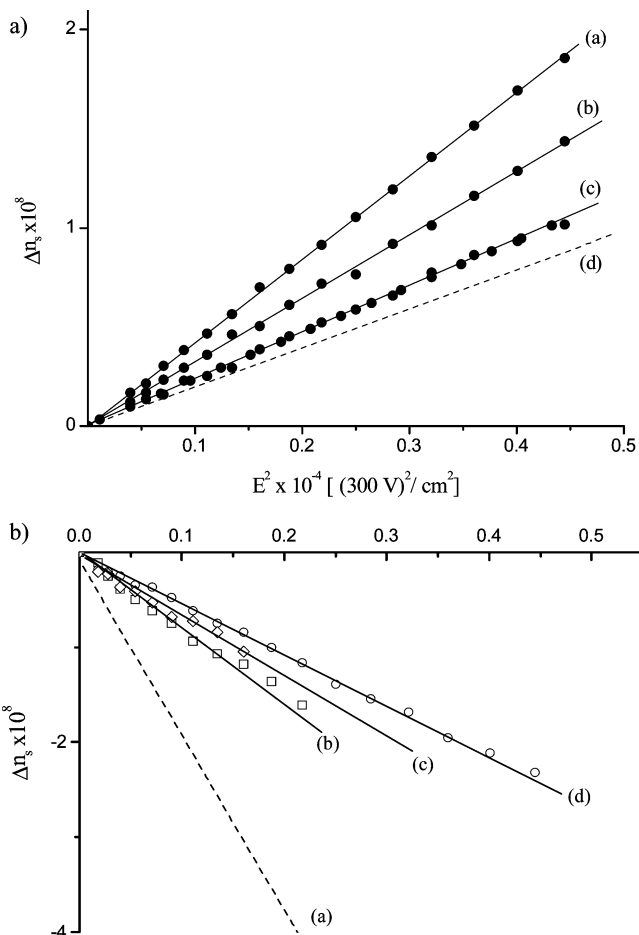


Figure 5. Variation of optical birefringence (Δn_s) vs E^2 for (a) **1** in benzene at different concentrations, (curve a) $2.351 \times 10^{-2} \text{ g}\cdot\text{cm}^{-3}$, (curve b) $1.294 \times 10^{-2} \text{ g}\cdot\text{cm}^{-3}$, and (curve c) $0.378 \times 10^{-2} \text{ g}\cdot\text{cm}^{-3}$, where curve d corresponds to pure solvent, and (b) for DAB-dendr-(alkyl chain)₈ in chloroform at different concentrations, (curve b) $2.86 \times 10^{-2} \text{ g}\cdot\text{cm}^{-3}$, (curve c) $3.11 \times 10^{-2} \text{ g}\cdot\text{cm}^{-3}$, and (curve d) $3.57 \cdot 10^{-2} \text{ g}\cdot\text{cm}^{-3}$, where curve a corresponds to pure solvent.

in Figure 8 demonstrate a clear sensitivity of the electrooptical properties to the nature of the groups located at the periphery of the dendrimer.

According to the theory of the electrooptical Kerr effect for polar solid particles, which may be used as a model for the behavior of dendrimers in an electric field, the specific Kerr constant (K) in solution is proportional to the product of μ^2/M and optical anisotropy of the polarizability ($\Delta\alpha$):^{34,35}

$$K = \pi N_A (n_0^2 + 2)^2 (\epsilon_0 + 2)^2 \Delta\alpha (\mu^2/M) (3 \cos^2\beta - 1) / (1215k^2 T^2 n_0) \quad (3)$$

For polar particles of similar shape, if the Kerr constant (K)

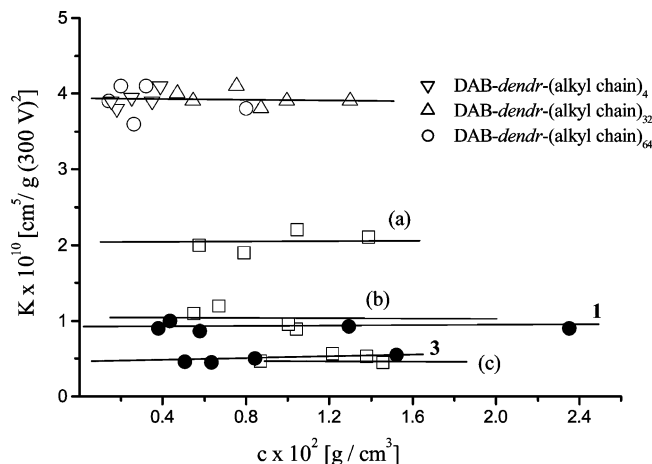


Figure 6. Variation of the specific Kerr constant (K) as a function of concentration for **1** and **3** (in benzene at 21 °C): (a) DAB-dendr-(CN)₄, (b) DAB-dendr-(CN)₃₂, and (c) DAB-dendr-(CN)₆₄ (in chloroform at 26 °C) and DAB-dendr-(alkyl chain)_n ($n = 4, 32$ and 64) (in chloroform at 26 °C).

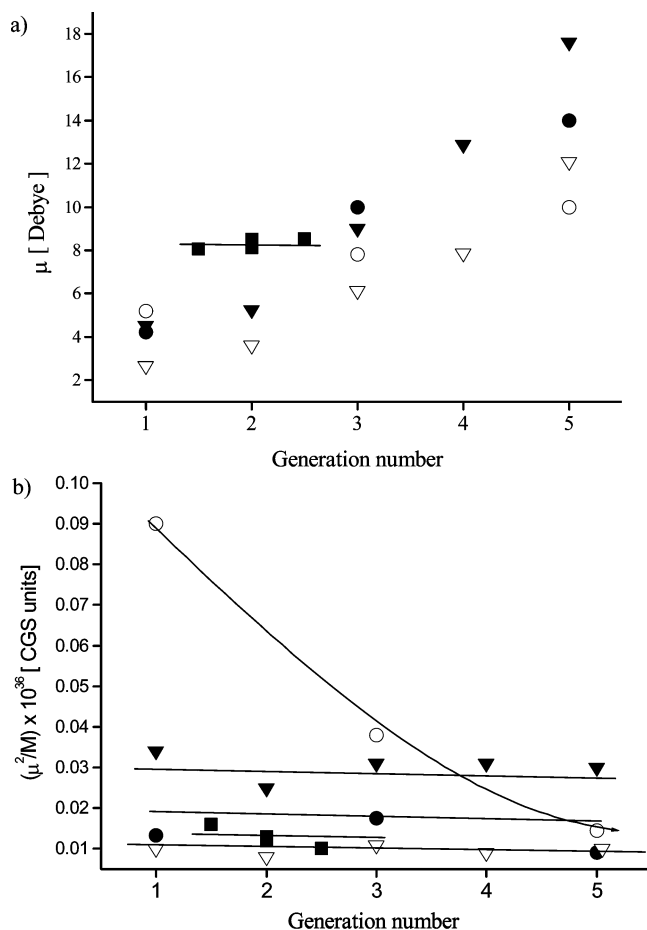


Figure 7. Variation of (a) dipole moment (μ) and (b) specific dielectric polarization (μ^2/M) as a function of generation number for (■) **1-4**, (○) DAB-dendr-(CN)_n, (●) DAB-dendr-(alkyl chain)_n, (▼) CN_n-[G_x]-[C]-[G_{x+1}], and (▽) [G_x]-[C]-[G_x].

decreases and the total dipole moment (μ) increases, there can be two explanations: (1) the shape symmetry of the particles increases, or (2) the optical anisotropies of polarizability ($\Delta\alpha$) are significantly different. However, it should be pointed out that $\Delta\alpha$ depends more strongly on the anisometry of the particles with the shape close to spherical than on the total dipole moment. It is known that $\Delta\alpha$ is closely related to the shape anisometry of ellipsoidal particles.^{31,34} Thus, for two kinds of

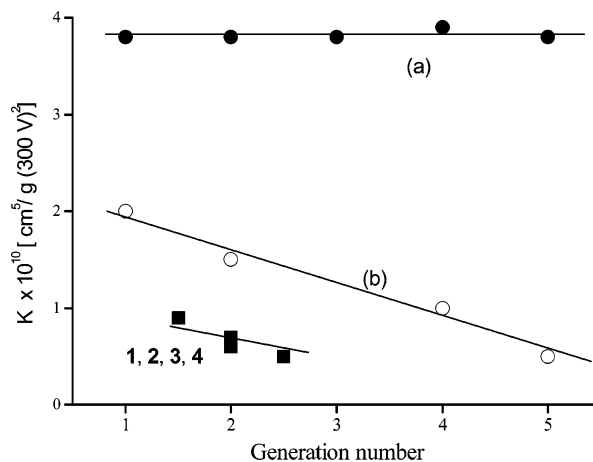


Figure 8. Variation of the specific Kerr constant (K) as a function of generation number for (a) DAB-dendr-(alkyl chain)_n and (b) DAB-dendr-(CN)_n and **1-4**.

particles with similar polarity and optical properties, but differing anisometry, the particles having the highest symmetrical shape will have the smallest Kerr constant.³⁴

The electrooptical properties (μ and K) obtained for DAB-dendr-(CN)_n (Table 3 and Figures 7a and 8) indicate that their molecular shape symmetry increases as dendrimer generation increases; this result can be explained by the fact that an increase in μ with an increase of the dendrimer generation leads to a decrease in K . This behavior is accompanied by a decrease of μ^2/M (Figure 7b), since K and μ^2/M are related as shown by eq 3.

On the basis of eq 3, the electrooptical behavior of DAB-dendr-(alkyl chain)_n and **1-4** were compared. The μ values of **1-4** are close to that of DAB-dendr-(alkyl chain)₁₆. However, the K values of **1-4** are smaller than those of DAB-dendr-(alkyl chain)_n by several orders of magnitude, but are close to that of DAB-dendr-(CN)₆₄, which has the highest symmetrical shape. Thus, we observe that **1-4** have a higher shape symmetry than DAB-dendr-(alkyl chain)_n, most likely, because of the shorter alkyl chains located on **1-4**.

Conclusion

These studies demonstrate the following: (1) compounds **1-4** have similar polarity and electrooptical characteristics despite the fact that they carry dendrons of different generations, indicating that in **1-4**, C₆₀ dictates the overall shape of the dendrimers, most likely, due to its location at the focal point of the macromolecule; (2) compounds **1-4** have total dipole moments similar to those of DAB-dendr-(CN)₁₆ and DAB-dendr-(alkyl chain)₁₆; (3) the high symmetry of **1-4** is responsible for their polar and electrooptical properties.

Acknowledgment. R.D. would like to thank the Swiss National Science Foundation (Grant no 200020-111681) for financial support.

Supporting Information Available: Text giving synthetic procedures and analytical data of **1-4** and structures of **5-8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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