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The symmetry of functionalized poly(propylene imine) dendrimers probed with hyper-Rayleigh scattering

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Abstract

Dendrimers are well-defined highly branched macromolecules that emanate from a central core and are synthesized through a stepwise, repetitive reaction sequence. In this study, different generations of a poly(propylene imine) dendrimer have been functionalized with second-order non-linear optical chromophores. The non-linear optical properties of these macromolecules have been investigated using the hyper-Rayleigh scattering technique. The sensitivity of this technique to molecular symmetry is exploited. The measurements show, in a unique way at the molecular level, that the dendrimers in solution form globular structures at generations with 32 and 64 4-dimethylaminophenylcarboxamide end-groups with restricted mobility of the end-groups.

1. Introduction

The interest in dendritic macromolecules originates from the unique properties of these hyper-branched structures that have a defined number of generations and functional end-groups [1,2]. The high degree of control over molecular weight and shape has led to the synthesis of unimolecular micelles [3], spherical and cone-shape mesostructures [4], as well as stratified dendrimers possessing generations of different structure [5]. More recently, dendrimers were used as functional catalysts [6] and guest–host systems [7]. Diameters of the spherical dendrimers range from 3 to 10 nm, enabling these structures to be ‘building blocks’ of a new chemistry set [8]. A variety of techniques have been used to study the three-dimensional architecture of dendrimers. Intrinsic viscosity measurements in conjunction with molecular-modelling studies have been used to verify the presence of globular structures [1]. More recently, transmission electron microscopy and scanning tunnelling spectroscopy have been used to verify the presence of globular structures at higher generations [2,8,9]. However, there are no reports of using molecular spectroscopy studies to probe the three-dimensional architecture of dendritic macro-

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molecules, other than ESR studies on modified PAMAMs [10,11]. Here, we report our results of probing appropriately modified poly(propylene imine) dendrimers [12] with hyper-Rayleigh scattering (HRS) [13–15].

2. Theory

In a hyper-Rayleigh scattering experiment, the intensity of the second-order scattered light \( I_{2\omega} \) that is generated by focusing an intense laser beam \( I_0 \) in an isotropic solution is measured. The intensity of the incoherently scattered harmonic depends on the different components of the molecular first hyperpolarizability tensor \( \beta \) which appears in the series expansion of the induced molecular dipole moment:

\[
\mu_i = \alpha_i E_j + \beta_{i,j,k} E_j E_k + \cdots ,
\]

assuming the electric dipole approximation [16,17]. From this equation, it is obvious that for centrosymmetric molecules all components of the second-order polarizability \( \beta \) vanish and hence no HRS signal can be observed. On a macroscopic scale, the induced dipole moment per unit volume (i.e. the polarization) at frequency \( 2\omega \) is given by:

\[
P_\omega(2\omega) = B_{ijk} E_j(\omega) E_k(\omega),
\]

\( B_{ijk} \) being the non-linear susceptibility tensor. In hyper-Rayleigh scattering from isotropic solutions, the necessary non-centrosymmetry on the macroscopic scale arises from orientational fluctuations of the individual non-centrosymmetric molecules that momentarily break the centrosymmetry of the solution. These orientational fluctuations play a similar role in second-order light scattering as the translational fluctuations (density fluctuations) do in linear light scattering. If the incident light travels in the \( x \)-direction with polarization in the \( z \)-direction and the scattered light is observed in the \( y \)-direction, the intensity of the second-order scattered light is given by:

\[
I_{2\omega} = g \langle B^2 \rangle I_{2\omega}^2 ,
\]

where \( I_{2\omega} \) is the intensity of the light at \( 2\omega \), \( \langle \cdot \rangle \) indicates orientational averaging and the factor \( g \) takes into account the scattering geometry and instrumental factors. For a two-component system, e.g. solute molecules in a solvent, and in the case of randomly oriented individual molecules, the averaged non-linear susceptibility is given as:

\[
\langle B^2 \rangle = F_{2\omega}^4 P_{2\omega}^2 \left[ N_S \langle \beta^2 \rangle_S + N_i \langle \beta^2 \rangle_i \right],
\]

\[
\langle \beta^2 \rangle = \langle \beta^2_{zzz} \rangle + \langle \beta^2_{xzz} \rangle ,
\]

with \( \beta_{zzz} \) in laboratory coordinates, \( F \) are local field factors at optical frequencies, and \( S \) (s) represents solvent (solute). The relation between \( \beta_{xyz} \) in laboratory coordinates and \( \beta_{uvw} \) in molecular coordinates \((u, v \text{ and } w \text{ are numbers})\) has been thoroughly described elsewhere [18,19]. \( \langle \beta^2 \rangle \) is the total averaged squared molecular hyperpolarizability. We use an external reference method, i.e. comparing the slope of a plot of \( I_{2\omega}/I_0^2 \) versus \( N_i \) for the sample with that for a reference molecule: para-nitroaniline (PNA) with \( \beta_{333} = 23 \times 10^{-30} \text{ esu} \) in chloroform [13,14] (all measurements are performed with chloroform as solvent). This approach effectively eliminates the need for the knowledge (or estimation) of the local field factors since these factors are divided out by measuring in nearly the same local field.

In a depolarization experiment, the second-harmonic signal is resolved into two orthogonal polarization components [19–21]. The depolarization ratio \( (\rho) \) is defined as the ratio between the intensities of the two components that are polarized parallel (along the \( z \)-axis) and perpendicular (along the \( x \)-axis) to the polarization of the fundamental beam (along the \( z \)-axis):

\[
\rho = \frac{\langle I_{2\omega,z} \rangle_z}{\langle I_{2\omega,x} \rangle_x} = \frac{\langle \beta^2_{zzz} \rangle}{\langle \beta^2_{xzz} \rangle} .
\]

Depolarization measurements on molecules with \( C_{2v} \) symmetry, e.g. PNA, with one dominant \( \beta \)-component \( (\beta_{333}) \), revealed depolarization ratios between 5 and 4 depending on the dominance of the major \( \beta \)-component. Octopolar groups, such as the \( D_{3h} \) group and the tetrahedral cubic group \( T_4 \) correspond to more isotropic objects than those belonging to lower-order or eventually polar groups, but are still compatible with \( \beta \)-properties. Such would not be the case for totally isotropic centrosymmetric groups like a sphere. Molecules belonging to these octopolar symmetry groups have a typical depolarization ratio of 1.5 [22,23].
3. Experimental

3.1. HRS apparatus

Laser pulses at a fundamental wavelength of 1064 nm are obtained from an injection-seeded, Q-switched Nd:YAG laser (Quanta Ray DCR3, 8 ns pulses, 220 mJ, 10 Hz). Fifteen percent of the energy of the fundamental beam is focused into a small cell (volume 7 ml). The intensity of the fundamental beam is varied by rotating a half-wave plate between two polarizers and is monitored with a photodiode. The harmonic light that is generated at the focal point is collected under 90° by a condenser system and is detected by a photomultiplier. Gated integrators are used to retrieve actual values for the intensities of fundamental and harmonic light. The fundamental beam is polarized perpendicular to the detection axis. For the depolarization measurements, the fundamental beam is also polarized perpendicular to the detection axis but the condenser system is replaced with a rotating analyser.

3.2. Materials

The NLO-modified dendrimers as well as the model compound N-n-propyl-4-dimethylaminobenzamide were fully characterized by IR, UV/VIS and NMR spectroscopy and the data are in full agreement with the structures assigned. The infrared spectra were recorded with a Perkin Elmer 1600 series FTIR using KBr pellets. The UV/VIS spectra were recorded on a Perkin Elmer UV/VIS Lambda 3B spectrophotometer using chloroform as solvent. The 1H NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.075 MHz. The details of the synthetic procedures will be presented elsewhere.

4. Results and discussion

4.1. Synthesis and characterization

The core of our modified dendrimers is based on poly(propylene imine) dendrimers (DAB-dendr-(NH2)x, with x = 4, 8, 16, 32 and 64 primary amine end-groups) which were synthesized by the divergent approach [12]. A variety of end-group modifications are reported [24]. For the present hyper-Rayleigh scattering study, we have modified the poly(propylene imine) dendrimers with 4-dimethylaminophenylcarboxamide end-groups to yield DAB-dendr-[NHCO-4-phenyl-N(CH3)2]x. These end-groups are typical donor-π-acceptor second-order non-linear optical (NLO) chromophores. The carboxamide end-groups were synthesized from the corresponding acid chloride and the amino end-groups of DAB-dendr-(NH2)x in yields of 70–80% (Fig. 1). The higher generations with 32 and 64 end-groups were purified by dialysis and the lower generations by extensive washing procedures.

The fifth-generation dendrimer, of which the structure is given in Fig. 1, still contains a small amount of impurity even after prolonged dialysis. This impurity is most probably 4-dimethylaminobenzoic acid that is clathrated within the interior of the dendrimer (5–10% of clathrate based on NLO end-groups as determined by 1H NMR spectroscopy). In addition, N-n-propyl-4-dimethylaminobenzamide, a model compound for a single chromophore, was synthesized.

Analysis of the UV/VIS spectroscopic data of the modified dendrimers and the model-compound (all with λmax = 290–300 nm) showed no significant electronic interaction between the chromophores of the dendrimers.

Analysis of the NMR spectra revealed a remarkable trend in the chemical shift of the amide proton (Fig. 2). Measured at concentrations of 0.1 mol eq. end-groups/liter, the chemical shifts are dramatically dependent on the generation, and hence on the local concentration of amides. For the model compound N-n-propyl-4-dimethylamino benzamide the amide proton is located at δ = 5.9 ppm, while an increase in the number of functional groups per molecule shifts the amide proton to lower field with a maximum chemical shift of δ = 8.0 ppm for the fifth generation. By performing the NMR experiments with samples of different concentrations, we found that the chemical shifts of the higher generations with 32 and 64 end-groups are concentration independent, while for the lower generations with 4, 8 and 16 end-groups and the model compound a concentration dependence is observed. It is generally accepted that hydrogen bonding will lead to a
DAB-dendr-(NH₂)₆₄ + ClO₃⁻ → NMe₂ CH₂Cl₂, NEt₃ → 70-80 %

Fig. 1. Functionalization of poly(propylene imine) dendrimers and a two-dimensional representation of DAB-dendr-(NHCO-4-phenyl-N(CH₃)₂)₆₄, a fifth-generation modified dendrimer.

deshielding of the proton involved and apparently the end-groups in the higher generations have a strong tendency to form intramolecular hydrogen bonds. This is the result of the close packing of end-groups at the periphery of higher generation dendrimers. This close packing also hampers the formation of intermolecular hydrogen bonding. At low generations, due to a less dense packing of end-groups and the higher mobility, intramolecular hydrogen bonds are less numerous and the possibility for intermolecular hydrogen bonds is higher.

4.2. Hyper-Rayleigh scattering

Using the HRS technique to measure the total averaged molecular hyperpolarizability of a dendrimer at different generations will probe both the tendency of the dendrimer to form spherical structures and the flexibility of these structures, due to the sensitivity of this technique to molecular (centro)symmetry. The non-linear light scattering consists of incoherent scattering from individual dendritic molecules. Therefore, the hyperpolarizability \( \beta_{\text{dendr}} = \sqrt{\langle \beta^2 \rangle_s} \) is determined for the whole dendritic structure and not for a single NLO end-group. These results are shown in Fig. 3. The hyperpolarizability of the dendrimer increases almost linearly with the number of chromophores for the lower generations. However, at higher generations this increase in hyperpolarizability becomes smaller and eventually disappears. This is clarified by Fig. 4 where the effective first hyperpolarizability \( \beta_{\text{eff}} \)
Fig. 2. Generation and concentration (insert) dependence of the chemical shift of the amide protons of DAB-dendr-(NHCO-4-phenyl-N(CH₃)₂)ₙ dendrimers and N-n-propyl-4-dimethylaminobenzamide (model for single NLO chromophore, ‘generation 0’) measured in CDCｌ₃. Generation 1, 2, 3, 4 and 5 correspond with 4, 8, 16, 32 and 64 end-groups, respectively. (Δδ = the difference in chemical shift with respect to the lowest concentration for the different dendrimers.)

per single NLO end-group is shown. This βₑff. was obtained by dividing the hyperpolarizability of the dendrimer (βdendr.) by the number of end-groups. The results of these HRS measurements are in full agreement with the expectation that the structure of the dendrimers becomes more spherical at higher generations. It should be noted that the experimental error in the measurement of the fifth-generation modified dendrimer is somewhat larger due to the presence of the clathrated impurity. However, this does not influence the trend observed. At low generations the high degree of conformational freedom allows the chromophores to arrange in a non-centrosymmetric way. Hence the hyperpolarizability of the dendrimer (βdendr.) increases as the number of chromophores is increased and βₑff. remains quasi unchanged. This is equivalent to what has been found for the case of side-chain functionalized polymers [25,26]. After the third generation the structure of the dendrimers becomes more spherical and the conformational freedom is restricted by steric hindrance due to the dense packing of the end-groups and in addition the formation of intradendritic hydrogen bonds [27]. Therefore, a further increase in hyperpolarizability is expected to be limited. Theoretically the first hyperpolarizability of a densely packed rigid, perfectly spherical and hence centrosymmetric dendrimer should be zero.

The results of depolarization measurements on some generations of the modified dendrimers and on N-n-propyl-4-dimethylaminobenzamide are given in Fig. 5. For the single N-n-propyl-4-dimethylaminobenzamide chromophore a depolarization ratio between 4 and 4.5 is measured, as expected. For the dendrimers, already for the second generation, a clear drop of the depolarization ratio to a value very close to 1.5, a typical value for the high-order symmetry groups corresponding to more isotropic structures, is observed. This is in contrast with the results of HRS measurements where the change in βₑff. of the chromophores with increasing dendrimer generation is less abrupt due to the flexibility of the den-
Fig. 5. Depolarization ratios for some generations of DAB-dendrimer (NHCO-4-phenyl-N(CH$_3$)$_2$)$_x$ and for a single N-n-propyl-4-dimetylaminobenzamide chromophore.

dendrimers. The depolarization measurements show that the average structure of the dendrimers is already isotropic at lower generations. Hence these measurements suggest that these dendrimers already possess a flexible but, on average, sphere-like structure at low generations and grow spherically for higher generations, becoming more rigid.

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