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Citation for published version (APA):

Put, E. J. H., Clays, K., Persoons, A. P., Biemans, H. A. M., Lijkx, C. M. P., & Meijer, E. W. (1996). Symmetry of functionalized poly(propylene imine) dendrimers probed with hyper-Rayleigh scattering. In G. R. Moehlman (Ed.), *Nonlinear optical properties of organic materials IX : 7-9 August 1996, Denver, Colorado* (pp. 122-131). (Proceedings of SPIE; Vol. 2852). SPIE. <https://doi.org/10.1117/12.256167>

DOI:

[10.1117/12.256167](https://doi.org/10.1117/12.256167)

Document status and date:

Published: 01/01/1996

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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The symmetry of functionalized poly(propylene imine) dendrimers probed with hyper-Rayleigh scattering

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ABSTRACT

Hyper-Rayleigh scattering has become the technique of choice for the determination of the first hyperpolarizabilities of non-linear optical (NLO) molecules. Moreover, by exploiting the sensitivity of this second-order NLO-technique to molecular and supra-molecular symmetry, this technique was upgraded to a powerful spectroscopic tool. We did this by probing the symmetry of NLO-functionalized dendrimers, measuring the first hyperpolarizability at different generations. These results are compared with measurements on side-chain NLO-functionalized linear co-polymers with different degrees of NLO-functionalization along the polymer backbone. 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 end-groups with restricted mobility of the end-groups.

Keywords: hyper-Rayleigh scattering, dendrimers, non-linear optics, macromolecules, second-order, hyperpolarizability.

1. INTRODUCTION

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 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 catalysts⁶ 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 and 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, to the best of our knowledge, there are no reports of using molecular spectroscopy studies to probe the three-dimensional architecture of dendritic macromolecules, other than ESR studies on modified PAMAM's.^{10,11} Here, we report on our results of probing appropriately modified poly(propylene imine) dendrimers¹² with hyper-Rayleigh scattering (HRS).¹³⁻¹⁵ These results are compared to HRS-measurements on side chain NLO-functionalized linear co-polymers with different chromophore loadings along the polymer backbone.

Hyper-Rayleigh scattering is a powerful tool to determine second-order non-linearities of molecules in solution. Moreover, measurements on bacteriorhodopsin^{16,17} and chiral NLO-polymers¹⁸ revealed that HRS is also an interesting tool to study supra-molecular architectures.

2. THEORY AND EXPERIMENTAL SECTION

2.1. THEORY

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

$$\mu_i = \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \dots \quad (1)$$

assuming the electric dipole approximation.^{19,20} From this equation, it is obvious that for centrosymmetric molecules all components of the second-order polarizability β 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 2ω is given by:

$$P_i(2\omega) = B_{ijk} E_j(\omega) E_k(\omega) \quad (2)$$

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:

$$I_{2\omega} = g \langle B^2 \rangle I_\omega^2 \quad (3)$$

where $I_{2\omega}$ is the intensity of the light at 2ω , $\langle \rangle$ indicates orientational averaging and the factor g takes into account 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:

$$\langle B^2 \rangle = F_\omega^4 F_{2\omega}^2 \left[N_s \left(\langle \beta_{zzz}^2 \rangle_s + \langle \beta_{xzz}^2 \rangle_s \right) + N_s \left(\langle \beta_{zzz}^2 \rangle_s + \langle \beta_{xzz}^2 \rangle_s \right) \right] \quad (4)$$

with β_{jzz} in laboratory coordinates, F are local field factors at optical frequencies, and S (s) represents solvent (solute). The relation between β_{xyz} in laboratory coordinates and β_{uvw} in molecular coordinates (u, v and w are numbers) has been thoroughly described elsewhere.^{21,22} For a scatterer with C_{2v} symmetry, e.g. *para*-nitro-aniline (PNA), assuming Kleinman symmetry these relations are given by:

$$\begin{aligned}\langle \beta_{zzz}^2 \rangle &= \frac{1}{7} \beta_{333}^2 + \frac{6}{35} \beta_{333} \beta_{322} + \frac{9}{35} \beta_{322}^2 \\ \langle \beta_{xxx}^2 \rangle &= \frac{1}{35} \beta_{333}^2 + \frac{2}{105} \beta_{333} \beta_{322} + \frac{11}{105} \beta_{322}^2\end{aligned}\quad (5)$$

This kind of linear dipolar molecules have only one dominant β -component (β_{333}), therefore one can simplify these equations to:

$$\begin{aligned}\langle \beta_{zzz}^2 \rangle &= \frac{5}{35} \beta_{333}^2 \\ \langle \beta_{xxx}^2 \rangle &= \frac{1}{35} \beta_{333}^2\end{aligned}\quad (6)$$

The total averaged squared hyperpolarizability is then given by:

$$\langle \beta^2 \rangle = \langle \beta_{zzz}^2 \rangle + \langle \beta_{xxx}^2 \rangle = \frac{6}{35} \beta_{333}^2 \quad (7)$$

All measurements are performed in chloroform as a solvent. We use an external reference method, i.e. comparing the slope of a plot of $I_{2\omega}/I_{\omega}^2$ vs N_s for the sample with that for a reference molecule, PNA with $\beta_{333} = 23 \cdot 10^{-30}$ esu in chloroform.^{13,14} 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.

One can only calculate molecular tensor-components for a molecule of which the symmetry is known. If the exact symmetry-group for the molecule under investigation is not known, as in this case, one can only determine the total averaged squared hyperpolarizability. Using the β_{333} of PNA as a reference, we therefore calculated the beta-values of the dendrimers as follows:

$$\beta_{\text{dendr.}} = \sqrt{\langle \beta^2 \rangle} = \sqrt{\frac{\text{slope}_{\text{dendr.}} \cdot \frac{6}{35} (23 \cdot 10^{-30} \text{ esu})^2}{\text{slope}_{\text{PNA}}}} \quad (8)$$

In a depolarization experiment, the second-harmonic signal is resolved into two orthogonal polarization components.^{22,24} The intensity of the second-order scattered light is then given by:

$$\begin{aligned}I_{2\omega,j} &= g \langle B_{jzz}^2 \rangle I_{\omega}^2 \\ \langle B_{jzz}^2 \rangle &= F_{\omega}^4 F_{2\omega}^2 \left[N_s \langle \beta_{jzz}^2 \rangle_s + N_s \langle \beta_{jzz}^2 \rangle_s \right]\end{aligned}\quad (9)$$

$I_{2\omega,j}$ is the intensity of the light at 2ω polarized in the j -direction. The depolarization ratio (ρ) is defined as the ratio between the intensities of the two components that are polarized parallel (along z -axis) and perpendicular (along x -axis) to

the polarization of the fundamental beam (along z-axis):

$$\rho = \frac{\langle I_{2\omega,z} \rangle_z}{\langle I_{2\omega,x} \rangle_z} = \frac{\langle \beta_{zzz}^2 \rangle}{\langle \beta_{xzz}^2 \rangle} \quad (10)$$

Combining Eq. 6 and Eq. 10 results in a depolarization ratio of 5. Depolarization measurements on molecules with C_{2v} symmetry, e.g. PNA, revealed depolarization ratios between 5 and 4 depending on the dominance of the major β -component (β_{333}). Octopolar groups, such as the D_{3h} group and the tetrahedral cubic group T_d correspond to more isotropic objects than those belonging to lower order or eventually polar groups, but are still compatible with β -properties.^{25,26} Such would not be the case for totally isotropic centro-symmetric groups like a sphere. Molecules belonging to these octopolar symmetry groups have a typical depolarization ratio of 1.5.

2.2. HRS SET-UP

Laser pulses at the 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 condensor system, consisting of a concave mirror and two lenses, 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 with no polarization in the detection system. The second-harmonic light scattering is discriminated from linear light scattering by a low pass filter and a 532 nm interference filter. It is important to note that these filters can not discriminate between the harmonic light scattering and fluorescence at 532 nm due to multi-photon absorption.²⁷ Therefore molecules that exhibit "multi-photon" fluorescence at 532 nm could not be measured with a fundamental wavelength of 1064 nm, until the recently developed time-resolved hyper-Rayleigh scattering.²⁸ For the depolarization measurements, the fundamental beam is also polarized perpendicular to the detection axis but the condensor system is replaced with a rotating analyser.

2.3. MATERIALS

All molecules 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.

3. RESULTS AND DISCUSSION

3.1. SYNTHESIS AND CHARACTERIZATION

The core of our modified dendrimers is based on poly(propylene imine) dendrimers which were synthesized by the divergent approach.¹² A repetitive reaction sequence using the double Michael addition of a primary amine to acrylonitrile followed by the heterogeneously catalyzed hydrogenation of the nitriles to primary amines, yields diaminobutane(DAB)-based poly(propylene imine) dendrimers (DAB-dendr-(NH₂)_x with x = 4, 8, 16, 32 and 64 primary amine end-groups).

A variety of end-group modifications are reported.²⁹ For the present hyper-Rayleigh scattering study, we have modified the poly(propylene imine) dendrimers with 4-methoxyphenyl imine end-groups to yield DAB-dendr-[NCH-4-phenyl-OCH₃]_x (1) and with 4-dimethylaminophenyl carboxamide end-groups to yield DAB-dendr-[NHCO-4-phenyl-N(CH₃)₂]_x (2). (Figure 1a) These end-groups are typical donor- π -acceptor second-order non-linear optical chromophores. The imine series 1 were synthesized by condensation of 4-methoxy-benzaldehyde and the amino end-groups of DAB-dendr-[NH₂]_x in toluene with yields of 67-73%. The carboxamide series 2 were synthesized from the corresponding acid chloride in yields of 70-80%. The higher generations with 32 and 64 end-groups were purified by dialysis and the lower generations by extensive washing procedures. The fifth generation dendrimers, of which the structure for the carboxamide series 2 is given in Figure 1b, still contains a small amount of an impurity clathrated within the interior of the dendrimer (5-10% of clathrate based on NLO end-groups as determined by ¹H-NMR spectroscopy) even after prolonged dialysis. In addition, N-*n*-propyl-4-methoxyphenyl imine and N-*n*-propyl-4-dimethylaminobenzamide, model-compounds for the single chromophores ("generation=0"), were synthesized.

Figure 1a: Functionalization of two series of poly(propylene imine) dendrimers, $x = 4, 8, 16, 32, 64$.

Figure 1b: Two-dimensional representation of DAB-dendr-(NHCO-4-benzene-N(CH₃)₂)₆₄

Analysis of the UV/Vis-spectroscopy data of the modified dendrimers and the model-compounds showed no significant electronic interaction between the chromophores of the dendrimers. Analysis of the NMR spectra of the carboxamide series 2 revealed a remarkable trend in the chemical shift of the amide-proton. 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 (Figure 2a). For the model-compound N-*n*-propyl-4-dimethylaminobenzamide the amide proton is located at $\delta = 5.9$ 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 $\delta = 8.0$ 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 (Figure 2b). It is generally accepted that hydrogen bonding will lead to a 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

Figure 2a: Generation dependence of the chemical shift of the amide-protons of the carboxamide series 2 and N-*n*-propyl-4-dimethyl-aminobenzamide ("generation = 0"). Generation 1, 2, 3, 4 and 5 correspond with 4, 8, 16, 32 and 64 end-groups, respectively.

Figure 2b: Concentration dependence of the chemical shift of the amide-protons of the carboxamide series 2 and N-*n*-propyl-4-dimethylaminobenzamide measured in CDCl₃. (Δδ = the difference in chemical shift in respect to the lowest concentration for the different dendrimers)

packing of end-groups and the higher mobility, intramolecular hydrogen bonds are less numerous and the possibility for intermolecular hydrogen bonds is higher.

3.2. HYPER-RAYLEIGH SCATTERING

Using the HRS-technique to measure the total averaged squared 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 symmetry. The non-linear light scattering consists of incoherent scattering from individual dendritic molecules. Therefore, the hyperpolarizability ($\beta_{\text{dendr.}}$) is determined for the whole dendritic structure and not for a single NLO-end-group. These results are shown in Figure 3a,b. For both series, the hyperpolarizability of the dendrimer increases almost linearly with the number of chromophores for the lower generations.

Figure 3a: The hyperpolarizability of different generations of DAB-dendr-[NCH-4-phenyl-OCH₃]_x (1)

Figure 3b: The hyperpolarizability of different generations of DAB-dendr-[NHCO-4-phenyl-N(CH₃)₂]_x (2)

Figure 4a: Evolution of the effective hyperpolarizability of the chromophores of serie 1 with the number of chromophores per dendrimer-molecule.

Figure 4b: Evolution of the effective hyperpolarizability of the chromophores of serie 2 with the number of chromophores per dendrimer-molecule.

However, at higher generations this increase in hyperpolarizability becomes smaller and eventually disappears. This is clarified by Figure 4a,b where the effective first hyperpolarizability (β_{eff}) per single NLO-end-group is shown. This β_{eff} was obtained by dividing the hyperpolarizability of the dendrimer ($\beta_{\text{dendr.}}$) by the number of end-groups ($\beta_{\text{eff.}} = \beta_{\text{dendr.}} / \# \text{ end-groups}$). 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. 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;

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 ($\beta_{\text{dendr.}}$) increases as the number of chromophores is increased and β_{eff} remains quasi unchanged. This is equivalent to what has been found for the case of side-chain NLO-functionalized

Figure 5: NLO-MA/DMA (A) and NLO-MA/MMA (B) side-chain NLO-functionalized co-polymers.

Figure 6: Evolution of β_{eff} for NLO-chromophores linked to a polymer backbone with increasing degree of NLO-functionalization along the polymer backbone.

linear polymers.³⁰ In Figure 5 the structures of two series of side-chain functionalized linear co-polymers, with two different NLO-chromophores covalently linked to a flexible linear poly(methylmetacrylate) backbone, are shown. The results of an HRS study on these co-polymers with different degrees of functionalization, given in Figure 6, show that the effective hyperpolarizabilities of both NLO-chromophores are not dependent on the degree of NLO-functionalization along the polymer backbone.

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, for the carboxamide series 2, the formation of intradendritic hydrogen bonds.³¹ 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.

Figure 7: A typical depolarization experiment on PNA

Figure 8: Depolarization ratios for some generations of DAB-dendr-(NHCO-4-phenyl-N(CH₃)₂)_x and for a N-*n*-propyl-4-dimethylaminobenzamide-chromophore.

The results of depolarization measurements on some generations of the carboxamide modified dendrimers 2 and on N-*n*-propyl-4-dimethylaminobenzamide are given in Figure 8. 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 the HRS measurements where the change of β_{eff} of the chromophores with increasing dendrimer generation is less abrupt due to the flexibility of the 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 the average, sphere-like structure at low generations and grow spherically for higher generations, becoming more rigid. In conclusion, we have presented results of HRS measurements on NLO-modified dendrimers and compared these results with HRS measurements on side-chain NLO-functionalized linear polymers. The sensitivity of hyper-Rayleigh scattering to (centro)symmetry has been put to use in support of the assumption that the dendrimers form globular structures at high generations with restricted mobility of the end-groups.

4. ACKNOWLEDGEMENTS

We wish to thank E.M.M. de Brabander-van den Berg for providing us with samples of the core poly(propylene imine) dendrimers. DSM Research and Philips Research are acknowledged for unrestricted research grants to the Eindhoven University of Technology. The work at the University of Leuven has been supported by the Belgian National Fund for Scientific Research (N.F.W.O.) (Grant 9.0012.92) and the Belgian Government (Grant IUAP-16). E.J.H. Put is financially supported by the Flemish Institute for Advancement of the Scientific and Technological Research in the Industry (I.W.T.). K. Clays is a senior research associate of the N.F.W.O.. H.A.M. Biemans is financially supported by the Netherlands Foundation for Chemical Research (SON), with aid from the Netherlands Organization for Scientific Research (NWO).

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