

UV SPECTRAL FEATURES OF POLY(PROPYLENE IMINE) DENDRIMERS

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The UV optical spectra of amine terminated poly(propylene-imine) (PPI) dendrimers of generations G1 to G5 were investigated experimentally. The occurrence of double band at (270–290) nm in absorption spectra of amine terminated dendrimer and the dependence of the spectra on the generation number and concentration in dichloromethane solution were discussed. The lineshape of double band was similar in the sequence G1 to G5, though some redistribution of the intensity of components was observed. A linear dependence of the absorbance in the double band was determined in the solutions at low concentrations of order $1 \cdot 10^{-5}$ M. Experimental data have indicated that double band is caused by several optical transitions related to the core electronic excitations. A significant Rayleigh light scattering was found for higher dendrimer generations.

Keywords: PPI NH₂-terminated dendrimers, optical absorbance, light scattering

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1. Introduction

Dendrimers are well-known monodisperse organic macromolecules, possessing spherical three-dimensional branched structures. Special interest is focused on pure poly(propylene-imine) dendrimers, which are the parent molecules of a large dendrimer family. The structural modifications of PPI dendrimers allow one to expect the formation of new materials with distinct physical properties [1]. The dendrimers, which have been functionalized with different types of chromophore groups, have shown unusual photophysical properties [2, 3]. Modified PPI dendrimers can be used as catalytic agents to control the growth of metal nanoparticles [4]. In biomedical applications, the dendrimers are promising materials in drug delivery systems [5, 6]. Also, differently modified dendrimer structures open new possibilities for scientific investigations [7] and applications in various industrial fields [8].

For instance, due to particular structural features, dendrimers are considered [9, 10] as efficient components in the solar cells. Therefore, the spectroscopic studies [11, 12] and analysis of electronic excitations are the pressing problems in scientific studies of dendrimers. To our knowledge, few spectroscopic data have been published concerning to the electronic excitation of the PPI dendrimer interior.

Amine terminated PPI dendrimers possess a regular structure starting from 1,4-diaminobutane (DAB) core molecule NH₂(CH₂)₄NH₂ to which four propylene-amine monomers C₃H₈N are added in the first generation G1 [13]. The aim of the present work was to study the main regularities in the optical properties of NH₂-terminated PPI dendrimers of generations G1 to G5. Fine structure of UV-vis spectra was analyzed in order to reveal the particular features which are useful for a deeper understanding of electronic excitations in dendrimers.

2. Experiment

Commercially available (Sigma-Aldrich) amine (NH_2) terminated PPI dendrimers of generations G1...G5 were studied by spectroscopic technique in the UV-vis spectral range. The gel-like substance of dendrimers was dissolved in dichloromethane. The obtained solutions (pH8) for generations G1 and G2 were transparent whereas significant light scattering was observed for G4 and G5. The transmittance of freshly-prepared solutions did not change during several hours.

The optical spectra of amine terminated dendrimer solutions in dichloromethane were measured in a UV-vis spectral range by means of a standard spectrophotometer (Perkin Elmer, Lambda 19). The parallel-walls quartz cuvettes of thickness up to 1 cm were used for spectroscopic investigations.

3. Results and discussion

Typical spectra of the optical density for G1 generation of amine terminated PPI dendrimer solutions in dichloromethane at various molar concentrations are presented in Fig. 1. The spectra characterize the total transmittance loss due to the absorption and scattering of light when passing the dendrimer solution. The absorption band at 270–290 nm is quite well resolved. The band intensity was found to increase linearly with an increase of the dendrimer molar concentration at low concentrations of order of 1×10^{-5} M. A weak broad peak

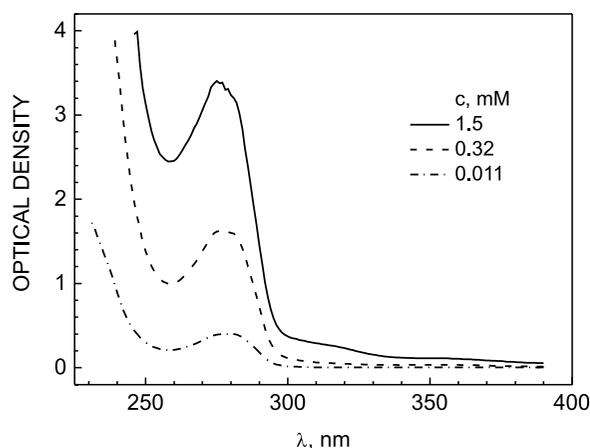


Fig. 1. Spectral dependence of the optical density of PPI amine terminated dendrimer (G1) solutions in dichloromethane at various molar concentrations c .

at ~ 315 nm was also detected at higher dendrimer concentrations. An occurrence of the absorption in the long wavelength region at 360 nm has been also noticed in the solutions of amine ($-\text{NH}_2$) and carboxylate ($-\text{COO}^-$) terminated [poly(amidoamine)] (PAMAM) dendrimers at higher concentrations (8.6×10^{-5} M) [14]. Below, we shall pay the main attention to the regularities in the optical spectra related to the peak at 270–290 nm.

The variation of the optical spectra of amine terminated PPI dendrimers of various generations is illustrated in Fig. 2. The spectra of solutions of the same weight concentration (0.1 mg/mL) and hence of various mole concentrations are shown for generations G1, G3 and G5. As in Fig. 1, the optical density has been measured in transmission mode and corresponds to the extinction represented by the contributions of both absorption and light scattering. As is seen in Fig. 2, at longer wavelengths ($\lambda > 330$ nm) the transmission losses are caused by dominating scattering.

The influence of light scattering increased substantially for larger generations G4 and G5. The

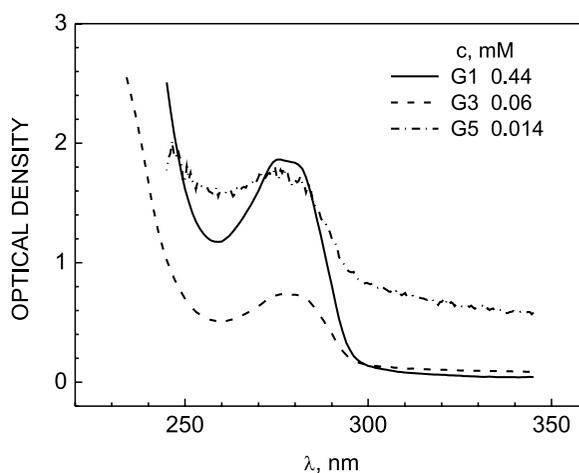


Fig. 2. Spectral dependence of the optical density of PPI amine terminated dendrimer solutions in dichloromethane at constant weight concentration 0.1 mg/mL corresponding to various mole concentrations c for generations G1, G3 and G5.

dominating contribution of light scattering for dendrimers solution of generation G5 is clearly illustrated in Fig. 3, in which the losses due to absorption have been excluded. As seen, there the spectral dependence of scattering loss agrees well with Rayleigh scattering law. A linear dependence of

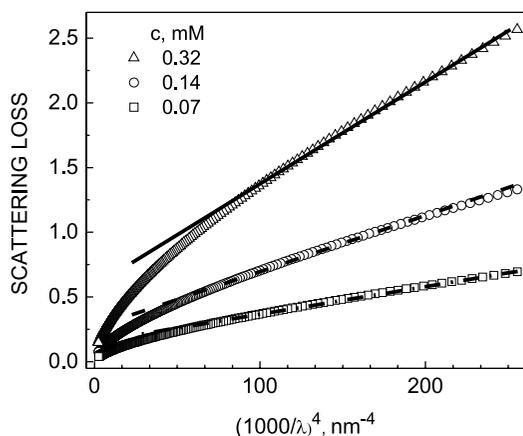


Fig. 3. Scattering loss, i. e., the optical density with absorption contribution excluded, versus λ^{-4} at various molar concentrations of amine terminated PPI dendrimer (G5) solutions in dichloromethane.

scattering loss versus λ^{-4} was observed in a wide spectral range with the slope increasing for higher dendrimer concentrations, though some influence of background absorption was still evident. An increase of light scattering in dendrimer solutions of higher generations is well understood taking into account a corresponding increase of viscosity [15] and the phase behaviour in amine terminated dendrimer solutions [16].

For a spherical particle of the diameter a , which is smaller by several orders of magnitude than the wavelength λ of incident electromagnetic radiation, the intensity I_s of light scattered from a beam of unpolarized light of intensity I_i is given by a well known formula for Rayleigh scattering [17]:

$$I_s = \frac{16\pi^4 a^6}{r^2} \frac{1}{\lambda^4} \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 (1 + \cos^2 \theta) I_i, \quad (1)$$

where m is the refractive index of the particle, θ is the scattering angle and r is the distance to the particle. Taking into account the radius of the particles for PPI dendrimer generations G1 to G5 [18], the relative intensity of Rayleigh scattering (1) was simulated using the MiePlot v. 4.2 software [19]. The calculated results of the Rayleigh scattering at the 400 nm by dendrimer particles are shown in Fig. 4. The simulated linear dependence

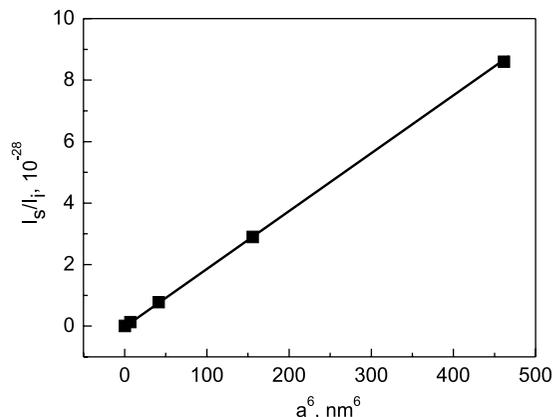


Fig. 4. The relative intensity I_s / I_i of Rayleigh scattering calculated according to (1) versus a^6 (where a is the diameter of dendrimer) for PPI dendrimers of generations G1 to G5 in dichloromethane at $\lambda = 400$ nm.

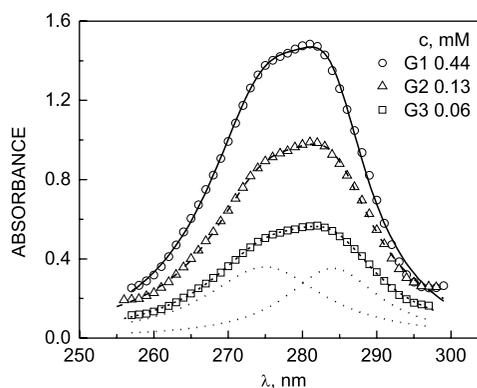


Fig. 5. Experimental (points) and simulated (curves) absorbance spectra, i. e., the optical density with the scattering contribution excluded, of amine terminated PPI dendrimers of generations G1, G2 and G3 at constant weight concentration 0.1 mg/mL corresponding to various mole concentrations c . The contribution of two components is shown for G3 generation.

is in agreement with the experimentally observed light scattering data.

The fine structure of the absorption band at 270–290 nm for PPI dendrimers was analyzed in the model of Lorentzian-type lines. In this spectral region, two peaks were clearly resolved (Fig. 5). The Lorentzian-type components of 20 and 14 nm width were observed at 275 and 284 nm, respectively. It should be noted that double band structure was also determined in the absorption spectra of a series of diamino-alkanes [20].

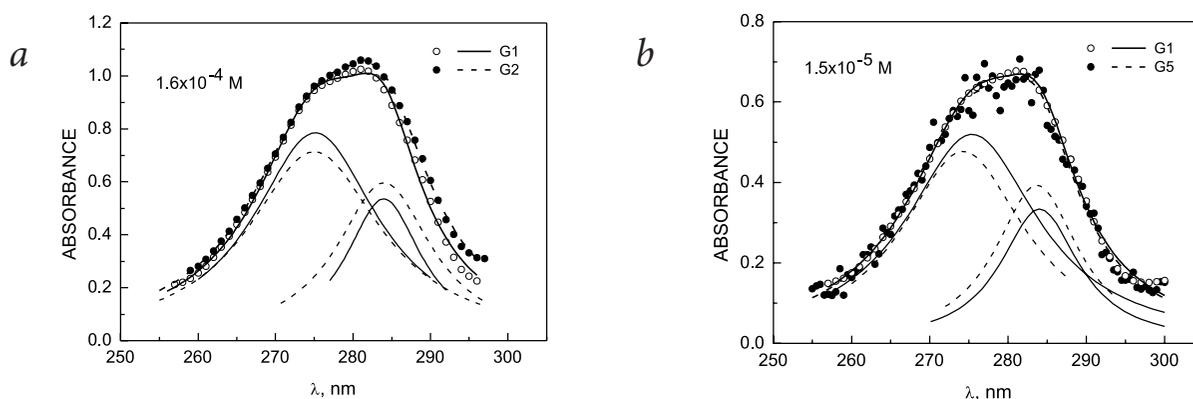


Fig. 6. Experimental (points) and decomposed (curves) absorbance spectra of amine terminated PPI dendrimer for generations G1, G2 and G5 at higher (a) and lower (b) molar concentrations.

The line shape of components in the double band was similar for all dendrimer generations. Figure 6 illustrates the fine structure of the double absorption band of amine terminated PPI dendrimer solutions. As seen there, the double band structure is close for various generations under consideration at the same molar concentrations. Thus, it is reasonable to assume that the excitation involving core is responsible for the absorption in the UV double band.

4. Conclusions

The absorption spectra of amine terminated PPI dendrimers of generations G1...G5 dissolved in dichloromethane were measured and analyzed. The double band has been observed in the wavelength range from 270 to 290 nm, which is typical of amine terminated PPI dendrimers. The fine structure of the double band is similar for all generations under investigation. It is also found that the role of the Rayleigh-type light scattering significantly increases for higher generations G3...G5 in agreement with the regularities in the size of dendrimer molecules. Based on the quantum-chemical calculations, the theoretical interpretation of amine terminated PPI dendrimers will be the subject of further investigations.

Acknowledgements

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POLI(PROPILENO-IMINO) DENDRIMERŲ UV SPEKTRŲ SAVYBĖS

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Santrauka

Ištirti įvairių generacijų (G1...G5) poli(propileno-imino) (PPI) dendrimerų, funkcionalizuotų amino grupėmis, tirpalų dichlorometane sugerties spektrai. Nustatyta būdinga visiems ištirtiems junginiams dviguba juosta ties 270–290 nm ir jos kitimas dėl dendrimerų generacijos ir

tirpalo koncentracijos. Gauta, kad sugertis priklausė tiesiškai nuo dendrimero molinės koncentracijos tirpale, esant nedidelėms 1×10^{-5} M koncentracijoms. Aukštesnės generacijos (G3...G5) dendrimerų tirpalai pasižymėjo didele sklaida, kuri atitiko Rayleigh sklaidos dėsnį.