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Infrared spectral characterization of poly(amidoamine) dendrimers peripherally modified with 1,8-naphthalimides

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Abstract

The present study describes the infrared characterization of some newly synthesized photoactive poly(amidoamine) dendrimers, whose peripheries have been modified with 1,8-naphthalimides. Main attention is being paid to the effect that different substituents at C-4 position of the naphthalene ring have upon the dendrimers polarization. Infrared studies have shown that the dendrimer generations have similar polarizations as the dendrimer molecules wherein no intermolecular hydrogen bonds occur.

Keywords: FT-IR spectroscopy; Poly(amidoamine); Photoactive dendrimers; 1,8-Naphthalimide

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1. Introduction

Dendrimers are hyperbranched, monodisperse, well defined three-dimensional macromolecules possessing a very high concentration of different functional groups [1–3]. In the last years fluorescent dendrimers of different types have been investigated intensively. The studies have been focused generally on their synthesis and applications [4,5]. Compounds with new properties and new areas of application are obtained as a result of binding fluorophores to the dendrimer structure [6].

Poly(amidoamine) (PAMAM) is a class of commercial dendrimers possessing different terminal functional groups [7–9]. In our previous investigations on the synthesis and the photophysical properties of some new zero and second generation PAMAM derivatives comprising 1,8-naphthalmide units in their periphery have been discussed [10–12]. Their fluorescence properties in the presence of different metal cations have been studied and the enhancement in their fluorescence intensity has been proved, which indicates these dendrimers have potentials as sensors for metal cations [10,12].

The present work reports on the infrared absorption of some new photoactive zero and second generation PAMAM dendrimers comprising 1,8-naphthalimides in their periphery. The effect of substituents at C-4 position of the naphthalene ring upon the infrared spectral characteristics is discussed. The dependence of the infrared frequency on dendrimeras generation has been investigated.

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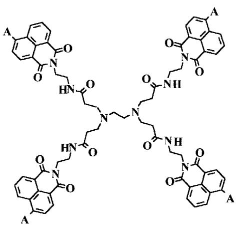
2. Experimental

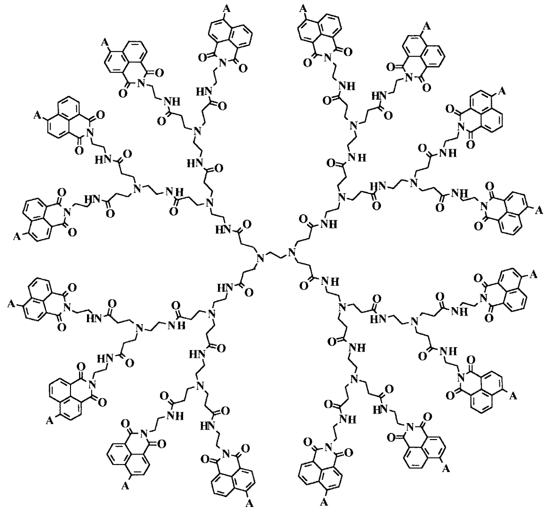
2.1. Materials and methods

Zero and second generations PAMAM dendrimers modified with 1,8-naphthalimide derivatives have the structures shown in the Schemes 1 and 2. Their synthesis has been published recently [10,11].

Commercial 20% PAMAM methanolic solution was subjected to evaporation under reduced pressure to obtain the pure dendrimer that was cast as a thin film. The IR spectra of all 1,8-naphthalimide labeled dendrimers were measured on a Bruker IFS-113v spectrometer at a 2 cm^{-1} resolution using KBr pellets.



Scheme 1. 1,8-naphthalimide-labeled PAMAM dendrimers **D1–D9**. A: H (**D1**); Br (**D2**); Cl (**D3**); NO_2 (**D4**); $NHCH_2CH=CH_2$ (**D5**); piperidine (**D6**); NHC_2H_5 (**D7**); n-NHC_6H_{13} (**D8**); $NHCH_2CH_2N(CH_3)_2$ (**D9**).



Scheme 2. 1,8-naphthalimide-labeled PAMAM dendrimers **D10–D15.** A: H (**D10**); NO_2 (**D11**); piperidine (**D12**); NHC_2H_5 (**D13**); n-NHC_6H_{13} (**D14**); $NHCH_2CH_2N(CH_3)_2$ (**D15**).

3. Results and discussion

Fig. 1 presents the infrared spectrum of PAMAM as a thin film. The absorption band characteristic for the vibration frequency of primary amino groups (NH_2) and the NH amide groups are at 3285 and 3356 cm^{-1}. The vibrations at 2936 cm^{-1} and 2842 cm^{-1} are characteristic for the aliphatic $-CH_2-$ groups. The amidic groups (HNC=O) from the dendrimer give absorption bands at 1635 cm^{-1} (amide I) and 1551 cm^{-1} (amide II).

The photophysical properties of the 1,8-naphthalimides depend upon the polarization of the naphthalimide molecule. The polarization occurs upon the irradiation resulting from the interaction between the substituents at C-4 position and the carbonyl group from the imide structure of the chromophoric system. The donor-acceptor interaction between the amino substituents at C-4 position (**A**) and the carbonyl groups (**C=O**) is given in Scheme 3. It illustrates as well the path of charge transfer of 1,8-naphthalimide labelled dendrimers.

Stretching and deformation vibrations of the main functions in the infrared region of PAMAM dendrimers from generation zero and PAMAM

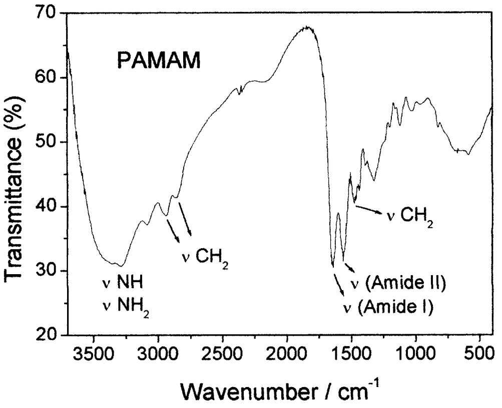
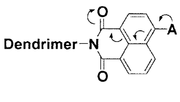


Fig. 1. Infrared spectrum of PAMAM dendrimer: zero generation (G0).



Scheme 3.

Table 1
Infrared absorption data of PAMAM generation zero (G0) and dendrimers **D1–D15** in cm^{-1}

	ν_{NH}	$\nu_{\mathrm{C-H}}$ arom	ν_{CH2}	$\nu^{\mathrm{AS}}_{\mathrm{C=O}}$	$\nu^{\mathrm{S}}_{\mathrm{C=O}}$	$\nu_{\mathrm{amide\ I}}$	$\nu_{\mathrm{amide\ II}}$	ν_{CNC} imide	$\delta_{\mathrm{C\text{-}H}}$ arom
PAMAM G0	3356 3285	–	2938 2862	–	–	1640	1560	–	–
D1	3373	3073	2962 2823	1699	1656	1625	1588	1188 1236 1384	778
D2	3383	3071	2951 2823	1700	1658	1614	1587	1185 1233 1344	780 750
D3	3386	3073	2947 2833	1709	1666	1627	1586	1344 1234 1183	786 760
D4	3387	3073	2958 2831	1707	1664	1625	1582	1189 1232 1365	786 759
D5	3328	3073	2941 2840	1682	1638	1616	1579	1243 1359	774 757
D6	3372	3073	2931 2846	1691	1651	1613	1587	1182 1235 1385	783 759
D7	3363	3076	2953 2853	1672	1632	1614	1575	1189 1245 1365	775 758
D8	3360	3080	2951 2851	1663	1635	1616	1582	1189 1235 1397	775 758
D9	3394	3073	2950 2849	1681	1637	1613	1581	1186 1394 1246	775 758
D10	3372	3073	2932 2827	1699	1658	1626	1589	1185 1236 1344	779
D11	3376	3076	2946 2829	1707	1664	1626	1583	1187 1233 1365	786 760
D12	3278	3072	2933 2820	1691	1648	1617	1586	1182 1234 1349	781 756
D13	3326	3069	2921 2827	1676	1639	1616	1577	1157 1242 1357	773 753
D14	3348	3085	2954 2928	1680	1638	1615	1581	1188 1243 1363	773 757
D15	3308	3072	2941 2820	1681	1643	1633	1578	1168 1241 1356	775 754

modified with different substituted 1,8-naphthalimides **D1–D15** are summarised in Table 1.

Fig. 2 presents the infrared spectra of 4-nitro-1,8-naphthalimide-PAMAM dendrimer (**D4** and **D11**) containing nitro (NO_2) groups. As seen, the absorption bands characteristic for the asymmetrical vibrations of nitro group appear at 1528 cm^{-1} while those for the symmetrical vibrations are at 1343 cm^{-1}.

Fig. 3 shows the region 1450–1750 cm^{-1} of the infrared spectra of the PAMAM dendrimers of zero generation. The C=O of the naphthalmides give rise to two absorption frequency bands. For the non substituted dendrimer **D1** these bands are at 1699 cm^{-1} and at 1656 cm^{-1}. The IR spectrum of 4-nitro-1,8-naphthalimide-PAMAM dendrimer (**D4**) has intensive absorption bands at 1707 cm^{-1} and 1664 cm^{-1}, respectively, due to the electron-accepting nature of the nitro group. After the substitution of the nitro groups with an electron-donating amino group, the absorption bands for 4-aminosubstituted - 1,8 - naphthalimide-PAMAM dendrimers (**D6** and **D8**) are shifted to the lower frequency region. The absorbances are at 1691, 1663 cm^{-1} and 1651, 1635 cm^{-1}, respectively. These bands are characteristic for the vibrations caused by the asymmetrical and the symmetrical carbonyl groups from the 1,8-naphthalimide chromophoric system. [13]. The difference between the symmetric and asymmetric vibrations assigned to the naphthalimides is 28–40 cm^{-1} (structures **1** and **2**) in Scheme 4.

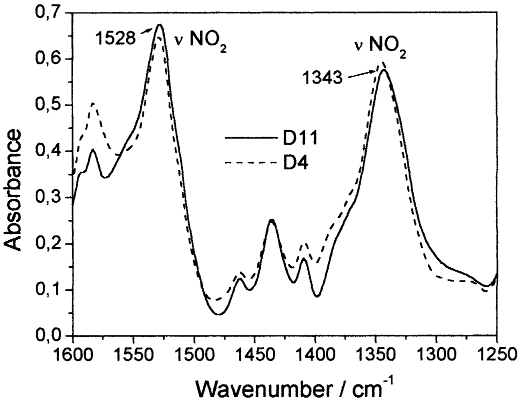


Fig. 2. Infrared spectra of 1,8-naphthalimide-PAMAM labelled dendrimers **D4** and **D11** in KBr pallets.

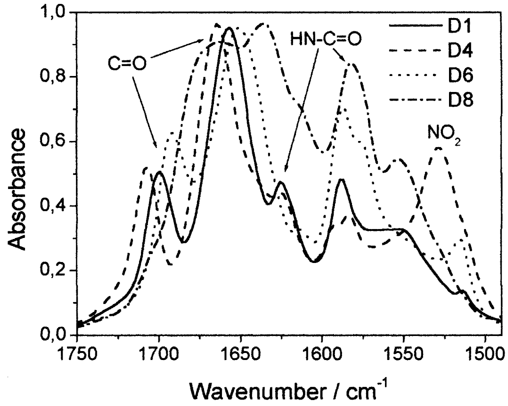


Fig. 3. Infrared spectra of 1,8-naphthalimide-PAMAM labelled dendrimers from zero generation in KBr pallets.

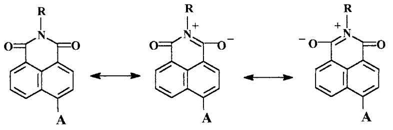
The high frequency C=O stretching vibration is assigned to the asymmetrical mode. The same are the signals assigned to the monomeric 1,8-naphthalimide derivatives [14–17]. The results show that the position of the absorption bands characteristic for the C=O groups depends on the nature of substituents at C-4 position while the dendrimer generation has a negligible effect.

Fig. 4 shows the dependence of the two C=O frequency bands of dendrimers **D1–D4** on the Hammett constants (σ), a linear correlation is obtained. The analytical form of the dependence is given by Eqs. (1) and (2):

$$\nu^{S}\ \left(\mathrm{cm}^{-1}\right) = 1659 \pm 6.10\sigma \tag{1}$$

$$\nu^{AS}\ \left(\mathrm{cm}^{-1}\right) = 1701 \pm 6.25\sigma \tag{2}$$

The comparison of the spectra mentioned reveals that the polarization of the 1,8-naphthalimide molecules has a strong effect upon the absorption properties of the chromophores. In the case of dendrimers **D4** and **D11** having an electron



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Scheme 4.

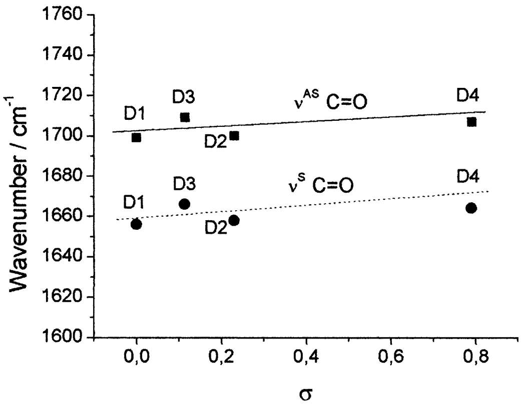

Fig. 4. Relationship between ν^S and ν^{AS} stretching vibrations and Hammett substituent constants σ for dendrimers **D1**–**D4**.

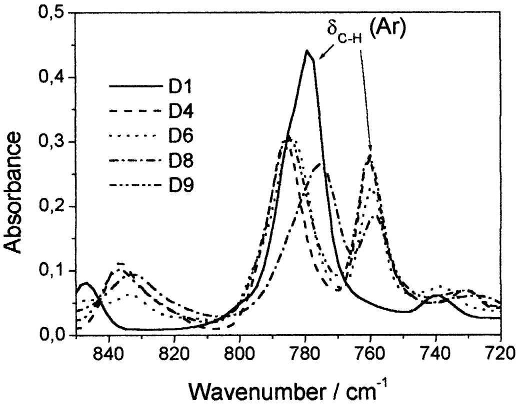

Fig. 5. Deformation vibrations (δ) of aromatic C–H bends of 1,8-naphthalimide-PAMAM labelled dendrimers from generation zero.

accepting nitro group the two bands, characteristic for the carbonyl frequency are shifted to the higher frequency region. Whereas in the case of dendrimers having electron donating amino groups at C-4 position of the naphthalene ring the respective bands are shifted to the lower frequency region.

The bands at 753–786 cm^{-1} are characteristic for deformation vibrations of the aromatic naphthalene rings (Table 1). There are single peaks in the spectra of the non substituted at C-4 position naphthalene rings: at 779 cm^{-1} (**D1**) and at 778 cm^{-1} (**D10**). After the substitution at C-4 position they have two peaks at 786–775 cm^{-1} and at 753–759 cm^{-1} region caused by the change in the polarization of 1,8-napthalimide molecules which is shown in Fig. 5 as well.

The 1,8-naphthalimide molecules contain an imide group (O=C–NR–C=O) in their six member rings. The absorption bands in the 1344–1397 cm^{-1} region are characteristic for the imide (C–N–C) bonds in the naphthalimde structure bonded to the dendrimer molecules. In the case of dendrimers **D4** and **D11** these bands are overlapped with the bands characteristic for the symmetrical vibrations of the nitro group. In this case the absorption bands are recorded as a shoulder. The infrared frequencies at 1157–1189 cm^{-1} and at 1232–1245 cm^{-1} are also assigned to the imide structures.

All dendrimers under study have aliphatic methylene (–CH$_2$–) groups in the dendrimer core. Their bands are at 2823–2851 cm^{-1} for the asymmetric and at 2931–2962 cm^{-1} for the symmetric stretching vibrations.

The amide groups of the dendrimer have absorption bands at 1613–1625 cm^{-1} (amide I) and 1581–1588 cm^{-1} (amide II). As seen after the modification of the dendrimer molecule with a 1,8-naphthalimide the bands characteristic for amide I are shifted to the higher frequency region ($\Delta\nu = 15$–27 cm^{-1}), whereas the bands characteristic for amide II are lower shifted ($\Delta\nu = 21$–28 cm^{-1}). This phenomenon is probably due to the different polarization of the dendrimer molecule after its binding to the 1,8-naphthalimide molecules.

Fig. 6 shows the exemplary the 600–1800 cm^{-1} range infrared spectra of 4-piperidino-1,8-naphthalimide-PAMAM dendrimer **D6** and **D12.** Both spectra are almost identical which is due to the similar polarization of the dendrimer molecules. This is another proof that the generation of the dendrimers does not affect their polarization. The determining factor in this process is the type of the fluorophore comprised in the dendrimer.

After the exchange of the nitro groups in **D4** with allylamino groups (**D5**) there are the peaks characteristic for the deformation stretching of ν_{NH} at 1540 cm^{-1}. The allylic group (CH$_2$CH=CH$_2$) at C-4 position of the naphthalene ring in 1,8-naphthalimide has characteristic bands at 920 cm^{-1} for the =CH$_2$ and 993 cm^{-1} for the =CH groups (Fig. 7).

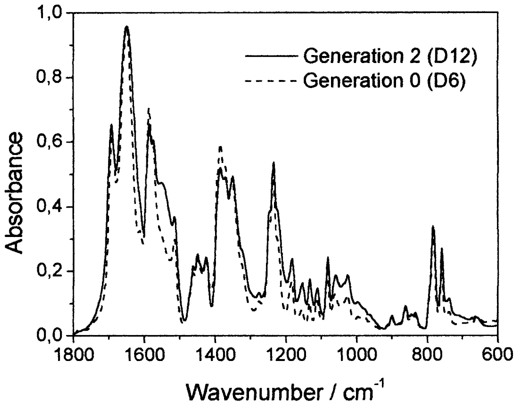

Fig. 6. Infrared spectra of 4-piperidino-1,8-naphthahmide-PAMAM labeled dendrimers **D6** and **D12**.

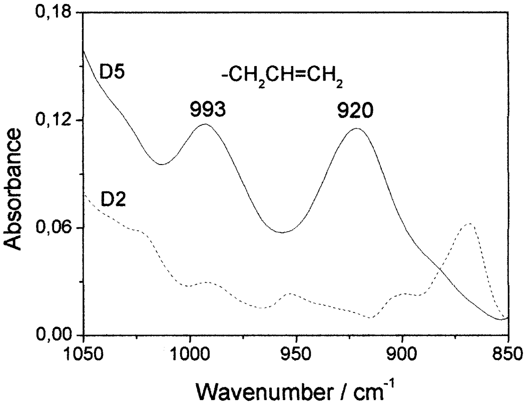

Fig. 7. Infrared absorption of allylic group in 4-allylamino-1,8-naphthalimide bonded to dendrimer **D5**.

4. Conclusion

The study presents the IR vibration and deformation frequencies arisen by 15 newly synthesized PAMAM dendrimers modified with 1,8-napthalimide derivatives. It has been shown that the mode of bonding the 1,8-napthalimide units to the PAMAM part affects the vibration frequencies assigned to amide I and amide II comprised in the dendrimer molecule. The substitutents at C-4 position of the 1,8-naphthalimide have an impact upon the vibration frequencies attributed to amide I and II, and to the carboxyl groups from the 1,8-naphthalimide fragments incorporated into the PAMAM molecule.

Acknowledgements

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