



Synthesis, Infra-red Study, and Application of Polyamidoamine Dendrimer Modified with 1,8-naphthalimide Derivatives as Novel Fluorescent Disperse Dye

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ABSTRACT

Infra-red spectroscopy is one of the most accessible and effective methods for identifying the newly synthesized compounds. In this paper the infrared characterization of photoactive polyamidoamine (PAMAM) dendrimers of zero, second and fourth generations modified with four different 1,8-naphthalimide derivatives were described. The effect of the dendrimer generations and various substituents at C-4 position of the 1,8-naphthalimide rings towards the dendrimers polarization were examined. Results have clearly shown that the dendrimer generations have negligible effect on molecules polarization. Meanwhile, the nature of the substituent at C-4 atoms of 1,8-naphthalimide rings and its capability to resonance with imide group strongly effect on the molecular polarization. This phenomenon might be attributed to the differences in the conjugational or migrating ability of the electrons from the PAMAM core to the peripheral 1,8-naphthalimides. Synthesize fluorescent dye was finally applied for dyeing of polyethylene terephthalate (PET) fabric and building-up properties, wash and light fastness were examined. Prog. Color Colorants Coat. 15 (2022), 203-211 © Institute for Color Science and Technology.

1. Introduction

The differences among the dendrimers, monomers, oligomers and hyper branched polymers have caused that their photophysical and photochemical properties investigated and reported [1-3]. Dendrimers are mono disperse, well defined three-dimensional macromolecules possessing a very high concentration of different functional end groups [4-6]. Recently, the fluorescent dendrimers with different structures have been considered extremely. Also, their synthesis and applications have generally been studied [7-8]. Polyamidoamine (PAMAM) dendrimers are the most common class of dendrimers which are produced

and commercialized with perfect structures possessing different terminal functional groups suitable for many materials and biotechnology [9-12]. Modified dendrimers with fluorescent chromophores have many applications in a wide range of areas especially in advanced technology [13]. Synthesis of dendrimers and their modification by 1,8-naphthalimide derivatives have been reported [14-17]. The potential of dendrimers modified with 1,8-naphthalimide compounds as a fluorescent cation sensor have also been investigated [18-20].

In the present work, the PAMAM dendrimer of zero, second and fourth generations were synthesized

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and modified with four different 1,8-naphthalimide chromophoric systems. The chemical structure of synthesized compounds was analyzed by infra-red spectrophotometry. The effect of different substituents at C-4 position of 1,8-naphthalimide rings and dendrimer generations on the polarization of molecules were verified.

2. Experimental

Polyamidoamine dendrimer of zero, second and fourth generations modified with 1,8-naphthalimide were synthesized according to our previously reported works [1, 2] in which the PAMAM core was covalently bonded to 4, 16 and 64 unites of naphthalimide respectively (Figures 1 and 2). PAMAM dendrimer was prepared by a divergent synthesis scheme using the reagent excess method starting from ethylenediamine by consecutive Michael addition and ester amidation reaction [1]. To prepare the full generation of dendrimer, ethylenediamine was dissolved in the methanol and cooled down in an ice bath. Then methyl acrylate was added dropwise at

continuous stirring to the dendrimer solution. The mixture was kept at room temperature for 168 hs. The excess of methyl acrylate and solvent were removed under vacuum at temperature below 50°C resulting in a nearly colourless viscous syrup. 1,8-Naphthalimide-conjugated dendrimer was synthesized from obtained PAMAM dendrimer of zero generation, which possesses four primary amine groups at periphery. For this purpose, 5-nitro-1,8-naphthalic anhydride was reacted with the primary amine end groups of dendrimer in ethanol solution by the condensation reaction. In this reaction 4-nitro-N-PAMAM-1,8-naphthalimide was synthesized. Treatment of 4-nitro-N-PAMAM-1,8-naphthalimide with stannous chloride in ethanol using hydrochloric acid leads to produce 4-amino-N-PAMAM-1,8-naphthalimide. 4-Acetylamino-N-PAMAM-1,8-naphthalimide was synthesized by reaction of 4-amino-N-PAMAM-1,8-naphthalimide with a mixture of acetic acid and acetic anhydride for 5 hs. All infra-red spectrum of modified dendrimers was measured on Nicolet 470/670/870 spectrophotometer using potassium bromide pellets.

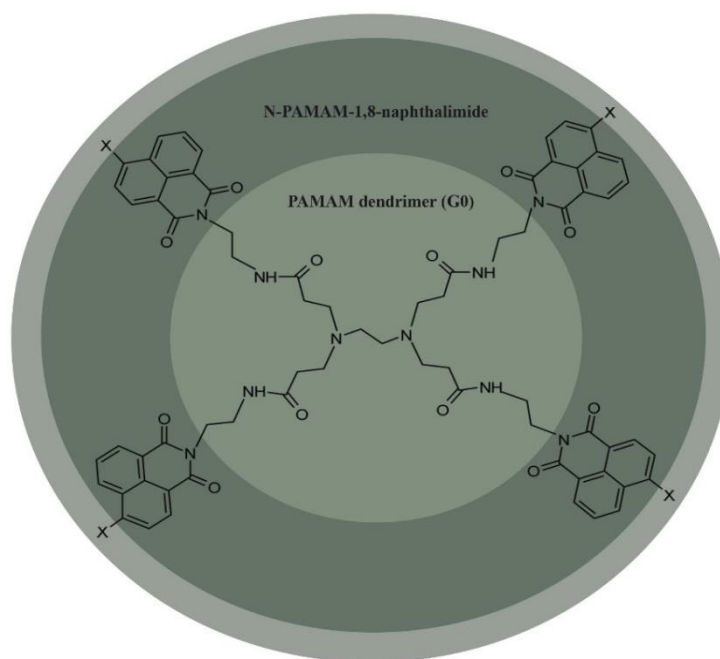


Figure 1: Polyamidoamine dendrimer of zero generation modified with 1,8-naphthalimide derivatives, A₁. (X=H), A₂ (X=NO₂), A₃ (X=NH₂), A₄ (X=NHCOCH₃).

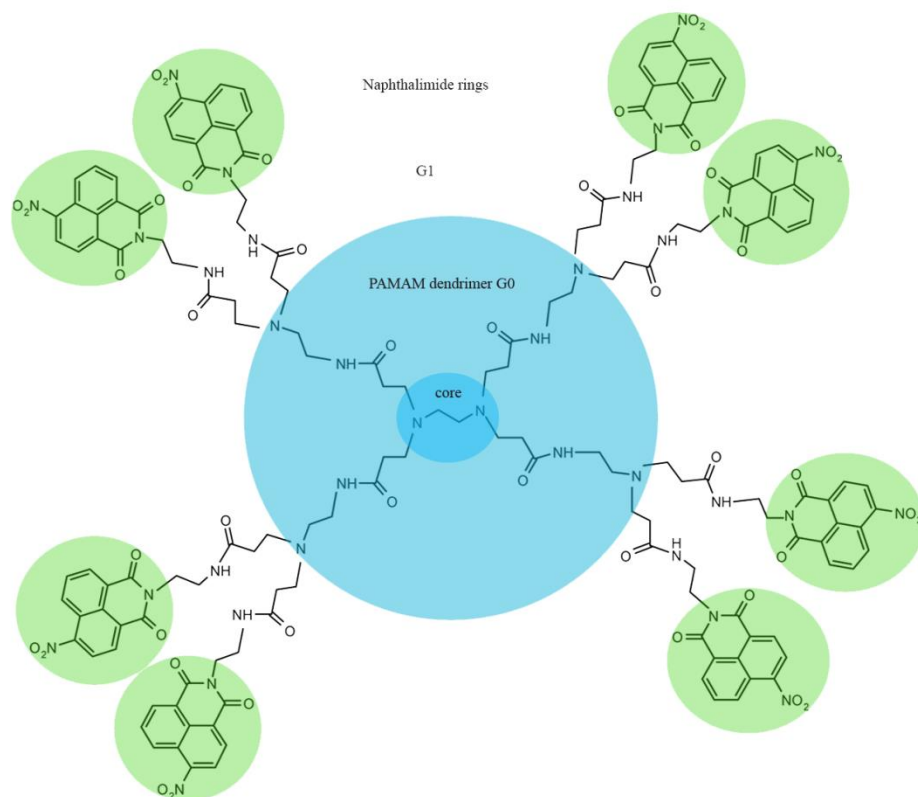


Figure 2: Polyamidoamine dendrimer of second generation modified with 4-nitro-1,8-naphthalimide.

3. Results and Discussion

Infra-red spectrum of polyamidoamine dendrimer of zero generation is shown in Figure 3. The absorption bands at 3285 and 3356 cm^{-1} are assigned to the vibration frequency of primary amino groups (NH_2) and the NH amide groups, respectively. Vibrations available at region 2937-2864 cm^{-1} are confirmed the presence of aliphatic CH_2 groups in the structure of the dendrimer compounds. The absorption peaks of amide groups have established in the region 1644 cm^{-1} (primary amid) and 1568 cm^{-1} (secondary amide). Photophysical properties of 1,8-naphthalimide compounds are dependent on their polarity. Polarity of these compounds are strongly related to the resonance accrued in substituent at C-4 position of naphthalimide ring and imide group. Mechanism of electron donating and electron accepting interactions between substituent at C-4 position and carbonyl groups of imide structure as well as generated resonance are presented in Figure 4. Stretching and bending vibrations existing in the infra-red spectrum of the polyamidoamine dendrimers modified with 1,8-naphthalimide derivatives are shown in Table 1.

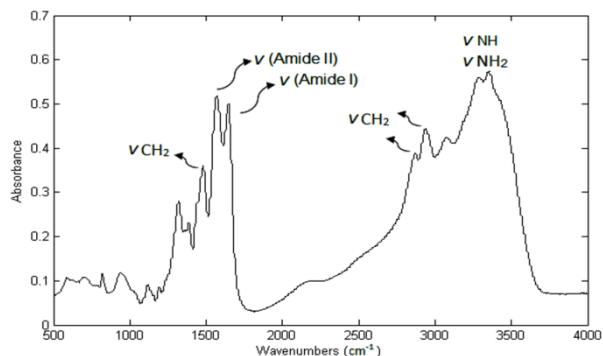


Figure 3: Infrared spectrum of polyamidoamine dendrimer of zero generation.

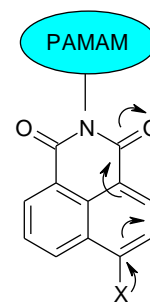


Figure 4: Mechanism of electron donating and electron accepting interactions between substituent at C-4 position and carbonyl groups of imide structure.

Infra-red spectrum of the polyamidoamine dendrimer of zero generation modified with 4-nitro-1,8-naphthalic anhydride is presented in Figure 5. As can be seen, the absorption bands of asymmetrical nitro groups have been appeared at 1526 and 1343 cm^{-1} . Figure 6 shows the infrared spectrum of PAMAM dendrimer modified with different derivatives of 1,8-naphthalimide. Carbonyl group ($\text{C}=\text{O}$) of the naphthalimide structures have been allocated two absorption frequency bands. These frequencies for the dendrimer modified with bare 1,8-naphthalimide (A_1) are at 1699 and 1659 cm^{-1} . While, these bands for the dendrimer modified with 4-nitro-1,8-naphthalimide (A_2) appeared at 1707 and

1664 cm^{-1} which could be attributed to the electron withdrawing nature of the nitro group. Substitution of the nitro groups by electron donating amino and acetylamino groups (A_3 and A_4) have shifted the absorption bands to the lower frequency at 1685, 1655 and 1645, 1636 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 [21]. The difference between the symmetric and asymmetric vibrations related to the carbonyl group of naphthalimide compounds is 28-40 cm^{-1} (Figure 7).

Table 1: Infrared absorption data of PAMAM dendrimers of zero generation (G_0) modified with 1,8-naphthalimide derivatives (A_1 - A_4) and PAMAM dendrimer.

Compounds	PAMAM (G_0)	A_1	A_2	A_3	A_4
ν_{NH}	3352 3280	3370	3408	3360	3361
$\nu_{\text{C-H aromatic}}$	-	3071	3077	3073	3072
ν_{CH_2}	2937 2864	2962 2823	2968 2832	2962 2823	2962 2850
$\nu_{\text{C=O}}^{\text{AS}}$	-	1699	1705	1677	1677
$\nu_{\text{C=O}}^{\text{S}}$	-	1656	1671	1636	1637
ν primary amide	1644	1625	1625	1608	1610
ν secondary amide	1568	1588	1581	1575	1577
ν CNC imide	-	1188	1186	1186	1185
		1236 1384	1232 1344	1243 1362	1246 1369
$\delta_{\text{C-H aromatic}}$	-	778	785 760	772 751	774 757

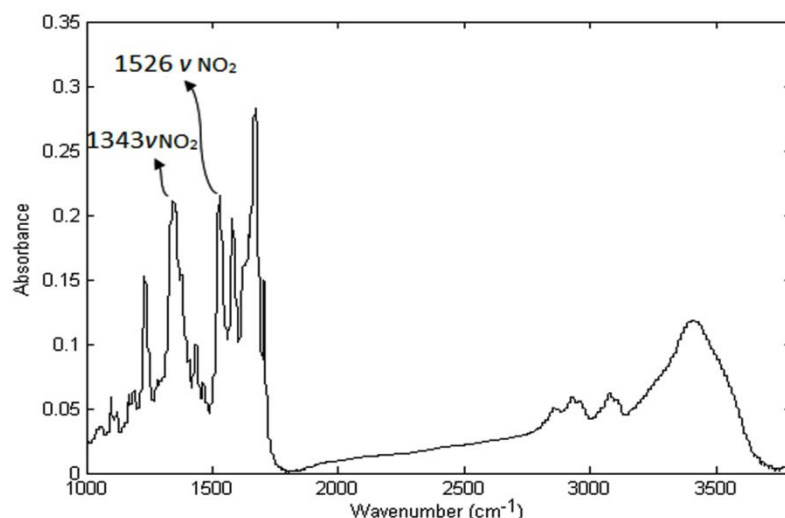


Figure 5: Infrared spectrum of polyamidoamine dendrimer of zero generation modified with 4-nitro-1,8-naphthalic anhydride (A_2).

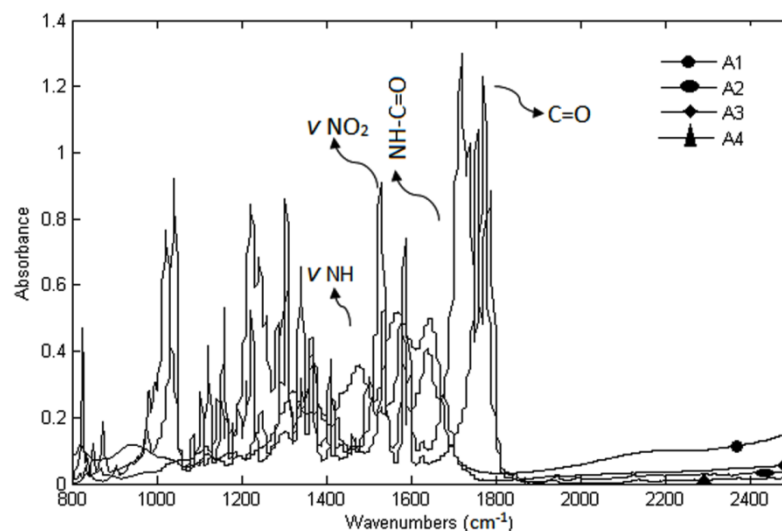


Figure 6: Infrared spectrum of PAMAM dendrimer modified with different derivatives of 1,8-naphthalimide (A₁-A₄).

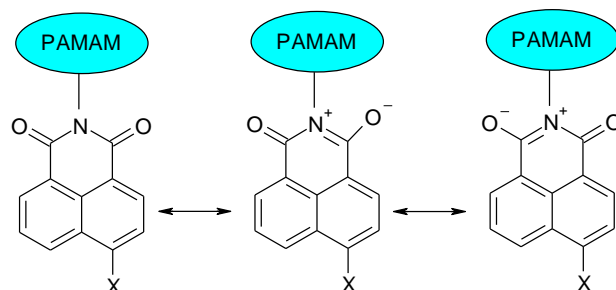


Figure 7: Symmetrical and asymmetrical carbonyl groups of naphthalimide compounds.

The highest frequency stretching vibration related to the carbonyl groups is assigned to the asymmetrical form [22, 23]. The results have shown that the substituent at C-4 position of naphthalimide ring has strong influence on the absorption frequency of carbonyl groups while these frequencies are independent of dendrimer generation. Analytical dependence of the two carbonyl frequency bands of dendrimers A₁-A₂ on Hammett constant (δ) obtained from the Eq.s 1 and 2 with a linear correlation have shown in Figure 8.

$$6.1 \delta \pm 1659 = \nu^S(\text{cm}^{-1}) \quad (1)$$

$$6.25 \delta \pm 1701 = \nu^{AS}(\text{cm}^{-1}) \quad (2)$$

As can be understood from the spectra, the polarization of 1,8-naphthalimide units has a great effect on the absorption behavior of the chromophoric systems. Therefore, the absorption peaks of the carbonyl group in compound A₂ containing electron accepting nitro group at C-4 position of 1,8-naphthalimide ring have moved to higher frequencies. Whereas, the respective bands have shifted to the lower frequency region in the dendrimer modified with 4-amino-1,8-naphthalimide units due to the electron donating properties of amino group. The bands assigned to deformation vibration of the aromatic naphthalimide rings have appeared at 751-785 cm⁻¹. Different polarization of the bare and C-4 substituted 1,8-naphthalimide molecules bonded to PAMAM dendrimer has caused the single peak related to deformation vibration of the aromatic naphthalimide rings at 778 cm⁻¹ while after substitution two peaks appeared at 772-785 cm⁻¹ (Figure 9).

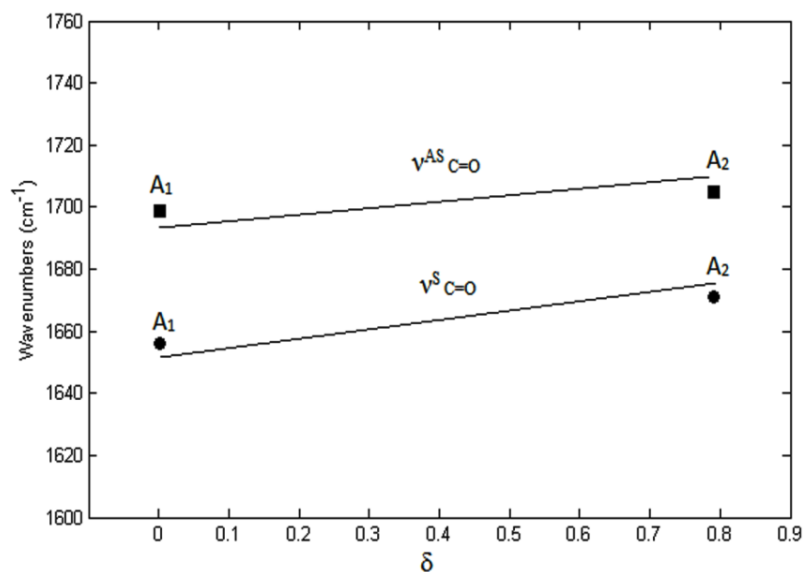


Figure 8: Correlation between ν^S and ν^{AS} stretching vibrations of carbonyl groups and Hammett substituent constants δ for dendrimers A₁-A₂.

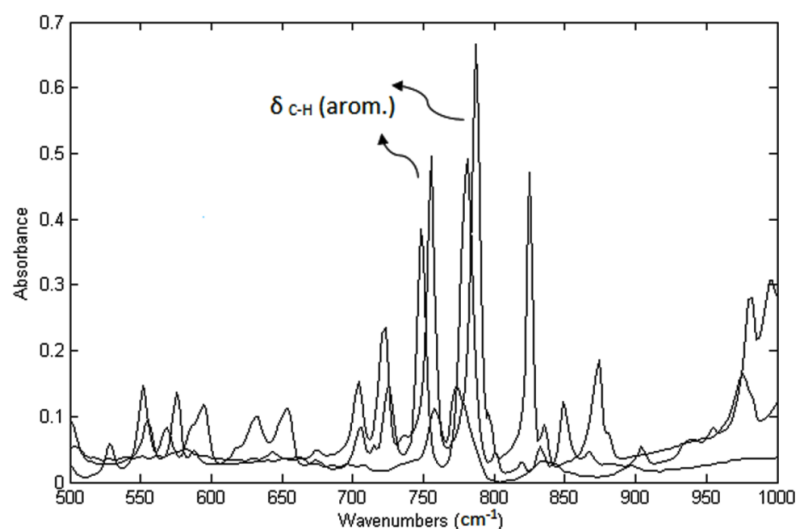


Figure 9: Deformation vibration (δ) of the aromatic C-H existing in N-PAMAM-1,8-naphthalimide rings.

The absorption peaks at region 1185-1188 cm^{-1} , 1232-1246 cm^{-1} and 1344-1384 cm^{-1} are characteristic to imide groups (CNC) bonded to dendrimers bone. It should be noted that, these peaks may have overlapped with the symmetrical vibration bands of nitro groups available at 4-nitro-N-PAMAM-1,8-naphthalimide. There are aliphatic methylene groups in the structure of the whole synthesized compounds which their asymmetrical and symmetrical stretching vibrations bands have appeared at 2823-2850 and 2962-2968 cm^{-1} , respectively. The absorption peaks assigned to the primary amide groups of the modified dendrimers

represented at 1608-1625 cm^{-1} while the respective bond for secondary amide groups appeared at 1575-1588 cm^{-1} . As can be found from the data presented in Table 1, the peaks of primary amide have moved to the higher frequency region ($\Delta\nu=19\text{-}32 \text{ cm}^{-1}$) while the respective bond related to secondary amide in modified dendrimers transferred to lower frequency ($\Delta\nu=8\text{-}20 \text{ cm}^{-1}$). This phenomenon could be explained by different polarization of the 1,8-naphthalimide units having various substituent at C-4 position bonded to the dendrimers. The 600-2700 cm^{-1} range of infra-red spectrum of zero, second and fourth generations of

PAMAM dendrimers modified with 4-nitro-1,8-naphthalimide molecules have shown in Figure 10. All the observed spectrums are almost similar to each other which is probably due to the same level of polarization of dendrimers. Therefore, the dendrimer generations have negligible effect on the polarization of synthesized compounds.

As the novel fluorescent disperse dye, preparation of dispersion of A₄ was done according to our previous works [24, 25]. The polyethylene terephthalate (PET) fabrics were pretreated and dyed based on the Figure 11 with the concentration of 0.1, 0.3, 0.7, 1, 1.2, 1.6, 2 and 4 % on the weight of fabric (o.w.f.). The building-up

curve of A₄ on PET fabric is shown in Figure 12. As it is clear, it reached the saturation at about 2 % concentration which is suitable for textile dyes. Wash and light fastness of the A₄ on the PET fabric were also determined and showed excellent wash (5) and light fastness (7-8). The light fastness of naphthalimide conjugated-PAMAM dendrimer is more than bare naphthalimide based disperse dyes which might be attributed to the fact that during the absorption of the light, its dendritic bone converts the light energy into fluorescence emission and reduced the destructive effect of the light [26].

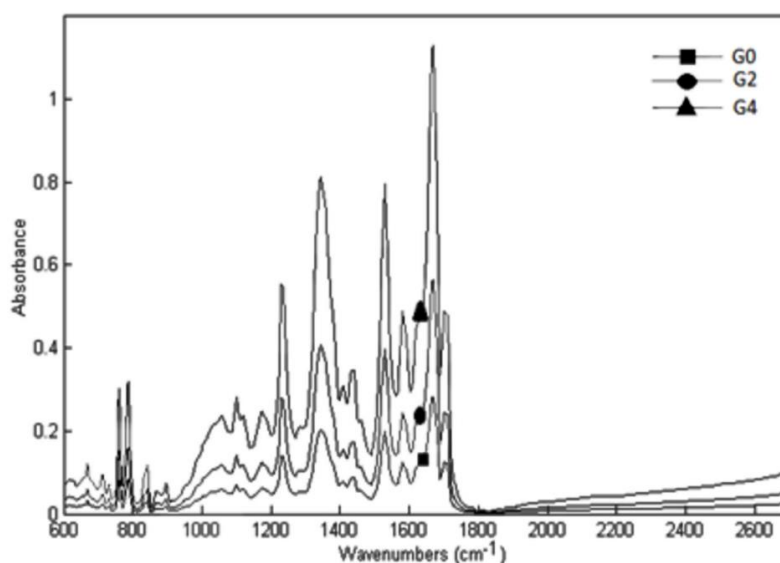


Figure 10: Infrared spectra of zero, second and fourth generations of PAMAM dendrimers modified with 4-nitro-1,8-naphthalimide molecules.

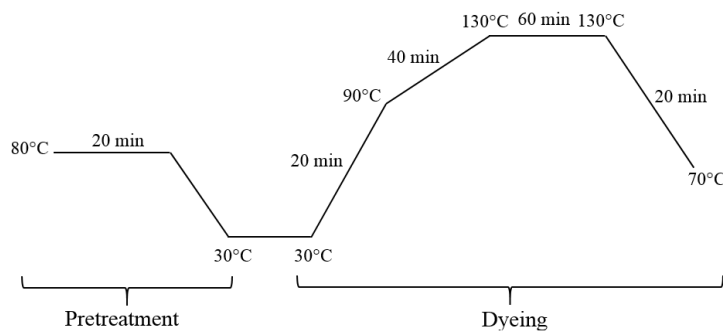


Figure 11: Pretreatment and dyeing curve of PET fabric with A₄.

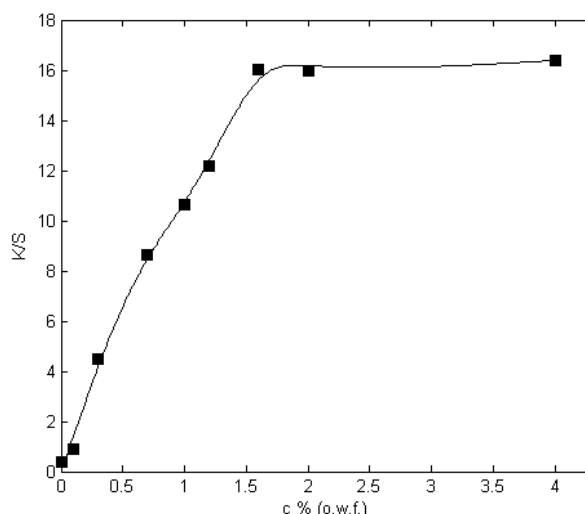


Figure 12: Building-up curve of A₄ on PET.

4. Conclusion

Four newly synthesized compounds by the modification of PAMAM dendrimer with 1,8-naphthalimide chromophoric systems were characterized using infra-red spectroscopy. The results showed that the modification of dendrimer with 1,8-naphthalimide derivatives have influenced on the polarization of molecules changing their vibrational frequencies at the infra-red spectrums. It was also found that the nature of the substituent at C-4 position of 1,8-naphthalimide rings

changed the vibrational stretching peaks of modified compounds. This phenomenon could be attributed to the differences in the conjugational or migrating ability of the electrons from the PAMAM tertiary amine to the different substituted peripheral 1,8-naphthalimides. Moreover, the negligible effect of dendrimer generations on the polarization of synthesized compounds was approved. The building-up properties of A₄ represented that it could be applied as an effective disperse dye for dyeing of PET fabric.

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