



The Synthesis of Poly(amidoamine) Dendrimer: Dyeing and Fluorescence Properties

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ABSTRACT

The synthesis of a new yellow fluorescent 4-(2-methylamino)-ethyloxy-N-PAMAM-1,8-naphthalimide from zero generation has been described. The chemical structure of synthesized dendrimers was confirmed using FT-IR, ¹HNMR and DSC techniques. The new materials are comprised of a 1,8-naphthalimide fluorophore having a substituent at C-4 position. The synthesized compounds (P2 and P3) were used for dyeing of wool fibers. The physical properties of the compounds (P2 and P3) were also investigated via fastness measurement. Prog. Color Colorants Coat. 11(2018), 173-178© Institute for Color Science and Technology.

1. Introduction

Dendrimers are highly branched molecules typically symmetric around a core with a three dimensional morphology. The presence of different functional groups at their outer shell enables them to react with other molecules [1]. Dendrimers have attracted much notice in the fields of conjugates, medical applications, diagnostics, host-guest chemistry, dendritic catalysts, and so on because of their multifunctional properties, such as well-defined chemical structure, good solubility, low viscosity, well-defined structure and abundant functional groups [2, 3]. Thus, the photoisomerization of dendrimers with photo-responsive cores, such as stilbene [4], azobenzene [5], diarylethene [6], has been studied.

Plasma treatment and a poly(propylene imine) dendrimer were employed to improve the dyeability of

wool fibers with cochineal natural dye by Sajed et al. Their results showed that the absorption kinetics of cochineal on raw, plasma-treated and dendrimer-treated fibers was best fitted with the pseudo-second-order model and the isotherms of the dyeing processes followed the Freundlich model [7]. Burkinshaw et al. found that the pre-treatment of cotton with a dendrimer could enhance the dyeability of the fiber with reactive dyes. The dendrimer contains primary amino groups, with which, theoretically, a reactive dye should be able to react under neutral/ acidic pH conditions. The effectiveness of the commercial levelling agent used suggests that there is the possibility of correction in the event of unlevel application of dendrimer and thus seems to offer an advantage over the reactive-type, cellulosic pretreatment compounds that have been developed [8]. Zolriasatein et al. used poly(amidoamine) (PAMAM) G-

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2 dendrimer for jute yarn. Jute yarns pretreated with PAMAM dendrimer displayed markedly enhanced color strength with reactive dyes, even when dyeing had been carried out in the absence of an electrolyte or a base. Dendrimer-treated jute yarn showed much better light-fastness than untreated one [9]. Khakzar et al. studied the effect of dendrimer on cotton dyeability with direct dye. Pretreatment of the cotton fabric with dendrimer in an emulsion form using pad-dry method followed by continuous dyeing markedly increased the color strength. Pretreatment of cotton fabric with poly(propylene imine) dendrimer enhanced its color strength using C.I. Direct Red 81 and C.I. Direct Blue 78. In addition, level dyeing was obtained, and no negative effects on the fastness properties of the dyes used were observed [10]. Zhang et al. synthesized water-soluble amino-terminated hyperbranched polymer from methyl acrylate and diethylene triamine by melt polycondensation. Dyed with reactive dyes, the treated cotton fabric displayed markedly enhanced color strength, even when dyeing had been carried out in the absence of the electrolyte. The washing fastness, rubbing fastness and levelling properties of the dyed, treated cotton fabrics were also compared with that obtained by conventional dyeing [11]. Sadeghi et al. presented a novel method for eco-friendly dyeing of cotton fabrics with direct dyes. Cotton fabric was modified with chitosan-poly (propylene) imines dendrimer (CS-PPI), and its dyeing and fastness properties were investigated using three direct dyes. It was concluded that the new eco-friendly process can help to considerably save time, energy, chemicals, and dyeing costs, and also can remedy the associated dyeing effluent problems from dyeing of cotton with direct dyes [12].

The present work aimed to synthesis and studied the pretreatment of wool fibers which could improve fluorescent properties of dyed fibers. The fluorescent and fastness (light and wash fastness) properties of treated fibers were investigated. Grafting treatment was performed in alcoholic media because of lower density of dendrimer than water.

2. Experimental

2.1. Materials and Instrumentation

All the organic solvents and Ethylenediamine (EDA), Methyl acrylate (MA) and acenaphthene were purchased from Merck Co. and used without further purification. The synthesis route and characterization of 4-amino-N-PAMAM-1,8-naphthalimide and 4-

acethylamino-N-PAMAM-1,8-naphthalimide have been described in our previous work [13, 14]. The wool fabrics were bleached with a solution containing 5 g/L sodium carbonate and 3 g/L non-ionic detergent (Labolene) under boiling condition for 2h, after which it was thoroughly rinsed and air dried at room temperature. UV-Vis and fluorescence spectra of the synthesized dendrimers were measured by Cecil 9200 double beam spectrophotometer and Ocean Optics Usb2000flg Fluorometer, respectively. Fluorescence quantum yields were determined on the basis of the absorption and fluorescence spectra using fluorescein as a standard ($Q_{ref} = 0.95$).

2.2. Synthesis of 4-(2-methylamino)-ethyloxy-N-PAMAM-1,8-naphthalimide

4-nitro-N-PAMAM-1,8-naphthalimide (0.46 g) was suspended in a mixture of 2-dimethylamino ethanol (20 mL) and potassium carbonate (0.55 g). The suspension was refluxed for 4 h. Then it was cooled down to room temperature and the resulting precipitate was filtered out. Yield: 77%; m.p: 211.8 °C; FT-IR (KBr) cm^{-1} : 3417 (N-H str), 2959 (C-H str. aliphatic), 1677 and 1585 (C=O str.); ^1H NMR (DMSO- d_6 , 500 MHz, ppm): 7.78-8.64 (20H, aromatic), 7.8 (6H, $\text{N}(\text{CH}_3)_2$), 3.25 (8H, CH_2NH), 2.71 (20H, $\text{NCH}_2\text{CH}_2\text{CO}$), 1.33 (12H, NHCOCH_3).

3. Results and Discussion

Schematic representation of the route for synthesis of the dendrimers is given in Figure 1. The bonding of 1,8-naphthalimides units to the periphery of PAMAM dendrimers gives the latter new interesting functional properties [15, 16]. 1,8-Naphthalimide has been chosen as fluorophore for the peripheral functionalization of various dendrimers because its photophysical properties can be easily modified. On the other hand, 1,8-naphthalimides are a medium sensitive chromophoric class whose fluorescence response based on the energy or photo-induced electron transfer can be used for sensors detecting environmental pollutants [17, 18]. The Modified dendrimers have been synthesized with 1,8-naphthalimide derivatives, as depicted in Figure 1. 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-substituted-1,8-naphthalimide units in its structure are obtained.

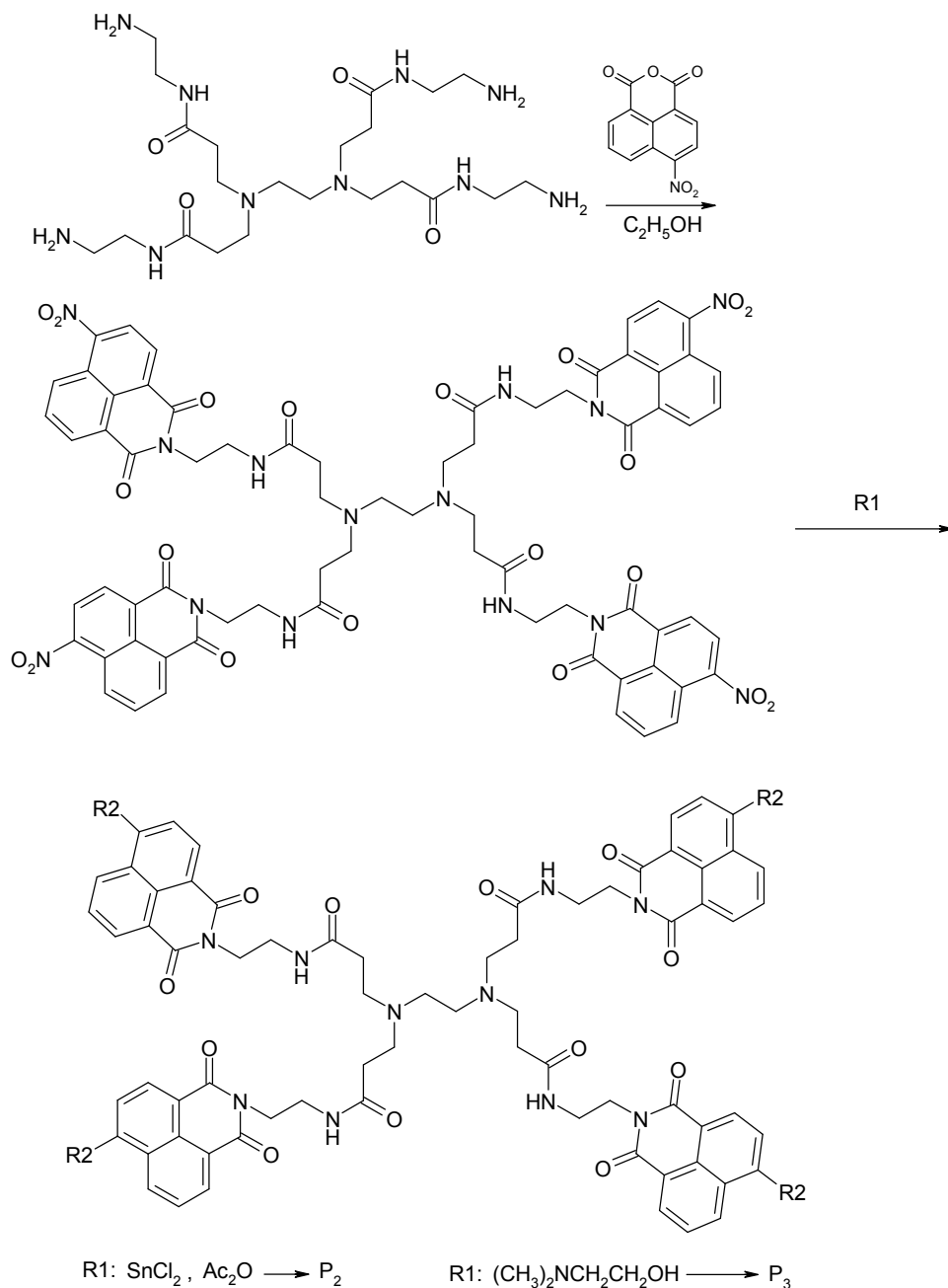


Figure 1: Synthesis of polyamidoamine dendrimers.

Treatment of 4-nitro-N-PAMAM-1,8-naphthalimide with stannous chloride in ethanol using hydrochloric acid leads to the production of 4-amino-N-PAMAM-1,8-naphthalimide. Two dendrimer derivatives were obtained from 4-nitro and 4-amino substituted naphthalimide. The chemical structures of all novel synthesized compounds were confirmed using DSC, FT-IR and ^1H NMR spectroscopy.

The bonding of fluorescent 1,8-naphthalimide units

to the PAMAM structure gives new interesting photophysical and photochemical properties. The basic photophysical properties of the monomeric 1,8-naphthalimides depend mainly on the polarization of 1,8-naphthalimide molecules. This is due to the electron donor-acceptor interaction between the substituents at C-4 position and the carbonyl groups from the imidic structure of the chromophoric system. On the other hand, it may be a result of the

environmental effect upon the interaction. Clearly, the absorption and emission bands of the 1,8-naphthalimide derivatives depend largely on the electron donating nature of the substituents at the C-4 position [19, 20]. Each fluorescence spectra has a fluorescence band with a single maximum, without vibrational structure [21, 22]. This is an indication of the prevailing fluorescence emission and of the unchanged molecular structure of the 1,8-naphthalimide fluorophore in the excited state [23, 24].

The synthesized compounds (P2 and P3) were applied at concentrations of 0.1%, 0.3%, 0.6%, 1%, 1.5%, 2.1% and 4.2% relative to the weight of wool fiber. The value of fluorescence (Figure 2) increased in the range of 0.1 to 2.4%.

The rubbing, washing fastness and light fastness data of the synthesized compounds are shown in Figure 3. It can be seen that all the compounds (P2 and P3) have excellent fastnesses.

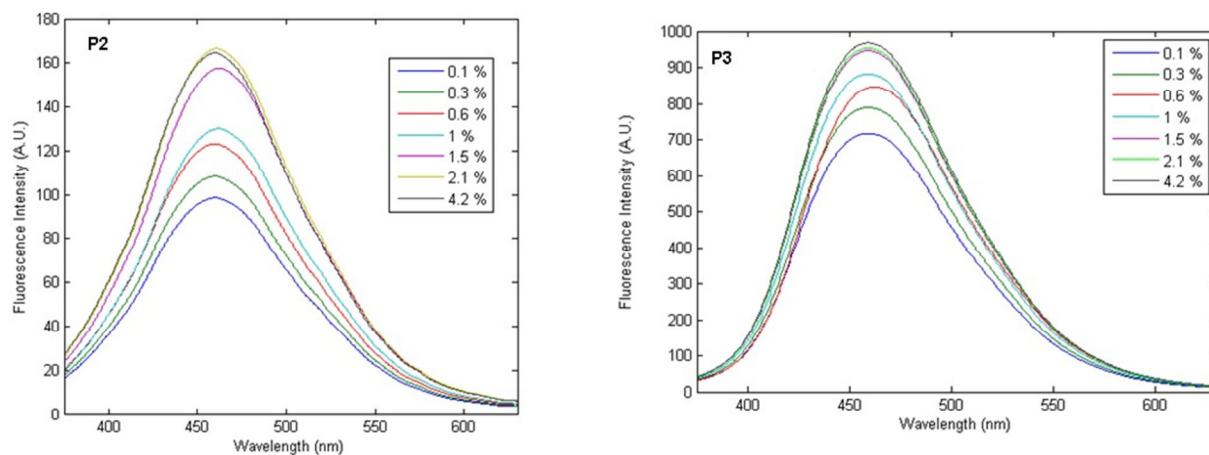


Figure 2: Fluorescence spectra of dyed fibers with modified dendrimer.

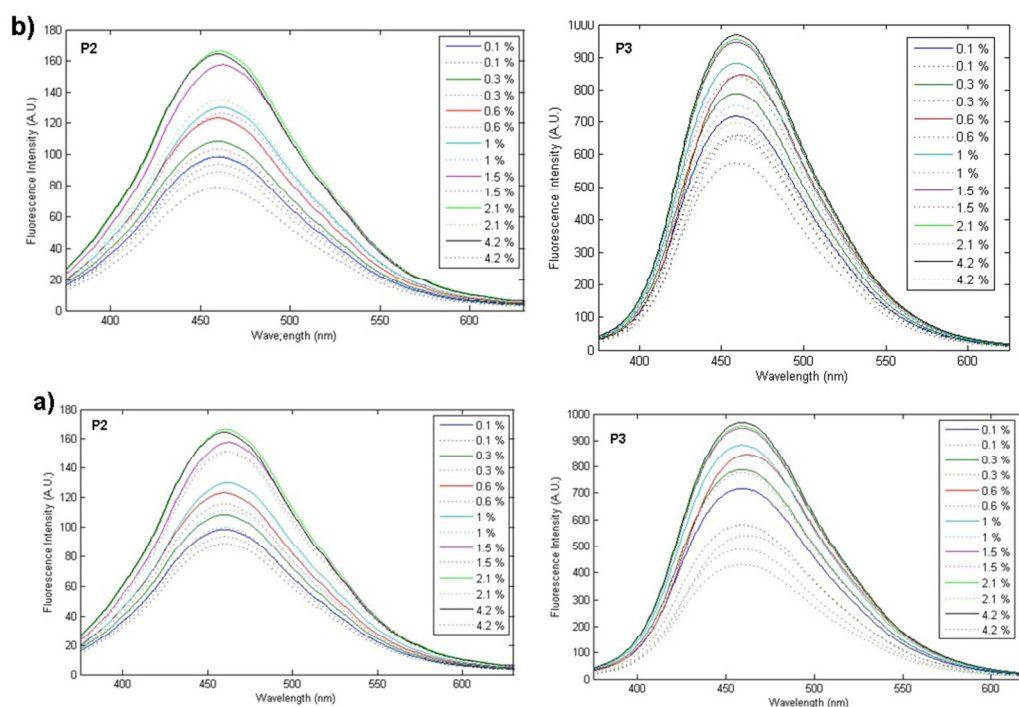


Figure 3: (a) light and (b) washing fastness of dyed fibers.

4. Conclusions

A new 4-(2-methylamino)-ethyloxy-N-PAMAM-1,8-naphthalimide with high yield and purity were synthesized and their photo-physical characteristics were studied on wool fibers. The final products have been obtained by nucleophilic substitution of nitro groups by 2-methylamino-ethyloxy. The substituted fluorescent dendrimers (P2 and P3) were used as fluorescence dyes on wool fibers. The bonding of fluorescent 1,8-naphthalimide units to the PAMAM structure gives new interesting photophysical and

photochemical properties. Each fluorescence spectra has a fluorescence band with a single maximum, without vibrational structure. Also, the synthesized compounds (P2 and P3) showed excellent dyeing properties in various fastnesses. Especially, the compound P3 showed a high degree of fluorescence and superior properties for wool fibers.

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5. References

1. M. Sadeghi-Kiakhani, A. R. Tehrani-Bagha, Retarding action of poly (amidoamine) dendrimers and cationic gemini surfactants in acrylic dyeing, *Dye Pigment.*, 125(2016), 323-330.
2. X. Fei, Y. Gu, Y. Lan, B. Shi, Fluorescent properties of novel dendrimer dyes based on thiazole orange, *J. Lumines.*, 131(2011), 2148-2152.
3. M. Jikei, M. Kakimoto, Hyperbranched polymers: a promising new class of materials, *Prog. Polym. Sci.*, 26(2001), 1233-1285.
4. T. Okamoto, A. Momotake, Y. Shinohara, R. Nagahata, T. Arai, Isomer Specific Solvent Effect on Photoisomerization of Photoresponsive Polyphenylene Dendrimers with a Stilbene Core, *Bull. Chem. Soc. Jpn.*, 80(2007), 2226-2228.
5. C. J. Gabriel, J. R. Parquette, Expanding Dendrons. The Photoisomerism of Folded Azobenzene Dendrons, *J. Am. Chem. Soc.*, 128(2006), 13708-10709.
6. Y. Fujimoto, T. Ubukata, Y. Yokoyama, Dendrimer diarylethenes: the memory effect of conformation in polymer matrices, *Chem. Commun.*, (2008), 5755-5757.
7. T. Sajed, A. Haji, M. Khajeh Mehrizi, M. Nasiri Boromand, Modification of wool protein fiber with plasma and dendrimer: Effects on dyeing with cochineal, *Inter. J. Biol. Macromol.*, 107(2018) 642-653.
8. S.M. Burkinshaw, M Mignanelli, P.E. Froehling, M.J. Bide, The use of dendrimers to modify the dyeing behaviour of reactive dyes on cotton, *Dye Pigment.*, 47(2000), 259-267.
9. A. A. Zolriasatein, M. E. Yazdanshenas, R. Khajavi, The application of poly(amidoamine) dendrimers for modification of jute yarns: Preparation and dyeing properties, *J. Saudi Chem. Rev.*, (2012), doi:10.1016/j.jscs.2012.01.007.
10. F. Khakzar, R. M. A. Malek, F. Mazaheri, The effect of dendrimer on cotton dyeability with direct dyes, *Chem. Ind. Chem. Eng. Q.*, 20 (2011) 379-385.
11. F. Zheng, Y. Chen, H. Lin, Y. Lu, Synthesis of an amino-terminated hyperbranched polymer and its application in reactive dyeing on cotton as a salt-free dyeing auxiliary, *Color Technol.*, 123(2007), 351-357.
12. M. Sadeghi-Kiakhani, S. Safapour, Salt-free dyeing of cotton fabric modified with prepared chitosan-poly (propylene) imine dendrimer using direct dyes, *Prog. Color Colorants Coat.*, 11(2018), 21-32.
13. M. Dodangeh, K. Gharanjig, M. Arami, Synthesis, characterization, and photo-physical properties of dendrimers modified with 1,8-naphthalimide derivatives as novel Fluorescent pH Sensors, *IEEE Sensor J.*, 14(2014), 2889-2896.
14. I. Grabchev, X. Qian, V. Bojinov, Y. Xiao, and W. Zhang, Synthesis and photophysical properties of 1,8-naphthalimide-labelled PAMAM as PET sensors of protons and of transition metal ions, *Polym.*, 43(2002), 5731-5736.
15. S. Yordanova, I. Grabchev, S. Stoyanov, I. Petkov, New detectors for metal cations and protons based on PAMAMdendrimers modified with 1,8-naphthalimide, *J. Photochem. Photobiol. A Chem.*, 283(2014), 1-7.
16. M. Liang, K. Wang, R. Guan, Z. Liu, D. Cao, Q. Wu, Y. Shan, Y. Xu, Several hemicyanine dyes as fluorescence chemosensors for cyanide anions, *Spectrochimica Acta A Mol. Biomol. Spect.*, 160(2016), 34-38.
17. I. Grachev, S. Dumas, J. Chovelon, A. Nedelcheva, First generation poly(propyleneimine) dendrimers functionalized with 1,8-naphthalimide units as fluorescence sensors for metal cations and protons, *Tetrahedron*, 64(2008), 2113-2119.
18. M. Hosseinnzhad, A. Khosravi, K. Gharanjig, S. Moradian, The comparison of spectra and dyeing properties of new azonaphthalimide with analogues azobenzene dyes on natural and synthetic polymers, *Arabian. J. Chem.*, 10(2017), S3284-S3291.
19. I. Grachev, J. Chovelon, V. Bojinov, G. Ivanova, Poly(amidoamine) dendrimers peripherally modified with 4-ethylamino-1,8-naphthalimide: synthesis and photophysical properties, *Tetrahedron*, 59(2003), 95-91-9598.

20. Y. Li, L. Cao, H. Tian, Fluoride ion-triggered dual fluorescence switchbased on naphthalimides winged zinc porphyrin, *J. Org. Chem.*, 71(2006), 8279-8282.
21. J. Y. Kim, C. Sakong, S. Choi, H. Jang, S. H. Kim, K. Seong Chang, M. S. Han, J. S. Lee, J. Pil Kim, The effect of fluorescence of perylene red dyes on the contrast ratio of LCD color filters, *Dye Pigm.*, 131(2016), 293-300.
22. M. Hosseinezhad, S. Rouhani, Characteristics of nanostructure dye-sensitized solar cells using food dyes, *Opto-Electron. Rev.*, 24(2016), 34-39.
23. H. Cao, V. Chang, R. Hernandez, M. D. Heagy, Matrix screening of substituted N-aryl-1,8-naphthalimides reveals new dual fluorescent dyes and unusually brightpyridine derivatives, *J. Org. Chem.*, 70(2005), 4929-4934.
24. M. Paula Militello, R. E. Hernández-Ramírez, I. V. Lijanová, C.M. Previtali, S.G. Bertolotti, E.M. Arbeloa, Novel PAMAM dendrimers with porphyrin core as potential photosensitizers for PDT applications, *J. Photochem. Photobiol. A Chem.*, 353(2018), 71-76.

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