ICC
Iranian Chemical Communication
Original Research Article
Payame Noor University of Ilamhttp://icc.journals.pnu.ac.ir

Synthesis and characterization of termini azobenzenedendrimer

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Received: 25 September 2013, Accepted: 12 October 2013, Published: 15 October 2013

Abstract

Some of the organic molecules can be isomerized upon photoirradiation and when they are accompanied by a change in the visible absorption spectrum, it can be called photochromism. Azobenzenes which are important parts of molecular machines and nanotechnology can be called photoisomerizationazobenzene (azo) chromophores, and have been incorporated into a wide variety of materials and molecular architectures, including polymers, dendrimers, and molecular glasses. We synthesized and characterized the AB_2 type polyamidoamine (PAMAM) dendrimers by single active site. PAMAM diazobenzenedendrimer was synthesized and characterized by FTIR and NMR (^1H, ^{13}C) and CHN-O Elementary analysis. A simple method can be used for the synthesis of azobenzene derivative PAMAM dendrimer and other similar compounds.

Keywords: Azodibenzoic acid, PAMAM dendrimer, termini group

Introduction

Some organic molecules isomerize upon photoirradiation. This phenomenon is called photoisomerization, and when accompanied by a change in the visible absorption spectrum, it is called photochromism. Azobenzenes are the important parts of molecular machines and nanotechnology [1,2]. Their former referent can be used as reversible optical information storage media, [3] optical switches,[4] control in LC molecules, etc. [5]. Dendrimer is an internationally accepted term. Dendrimers and dendrons are repeatedly branched and also can be regarded asmonodisperse and usually highly symmetric compounds. The first

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dendrimers were synthesised divergently by Vögtle in 1978 [6], Denkewalter and coworkers at Allied Corporation as polylysinedendrimers in 1981[7], Donald Tomalia atDow Chemical in 1983 [8] and in 1985 [9], Newkome in 1985[10]. In 1990, a convergent synthesis was introduced by Fréchet[11]. Azobenzenes were used at the end of a group of PAMAM synthesis by single active site [12,13]. The dendrimers are branched by diazobenzene synthesis and characterization.

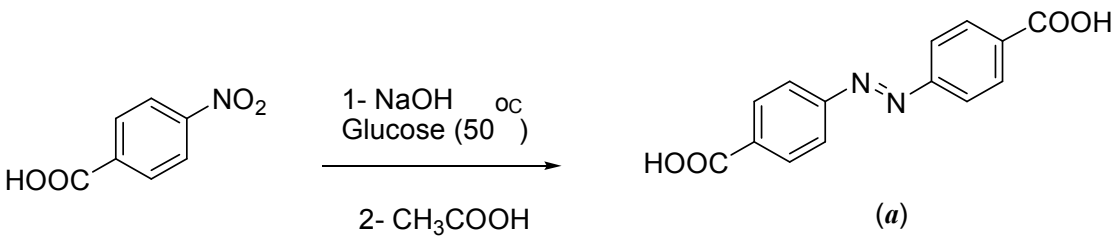
Experimental

General

IR spectra of the compounds were obtained on a Shimadzu IR-435 spectrometer using a KBr disk. The ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AQS 400 Advanced instrument at 400 MHz in dimethyl sulfoxide (DMSO-d6) using tetramethylsilane as an internal standard. All of the products are known compounds and are characterized by comparing the FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopic data and their melting points with the literature values. CHNO Elementary analytical has been obtained by Flash EA 1112 elementary analyzer.

General procedure preparation 4,4'-azodibenzoic acid

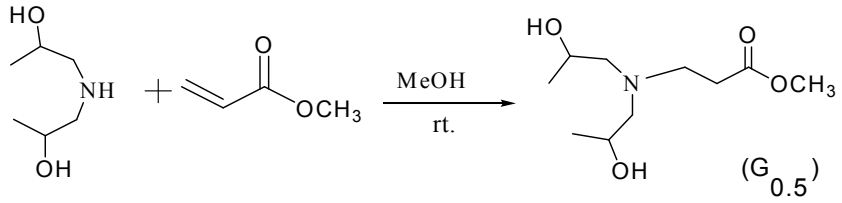
4-Nitrobenzoic acid was heated in sodium hydroxide solution at 50°C. A solution of glucose was added dropwise to this temperature with occasional shaking.The reaction mixture was then cooled to room temperature and then mixed for 8h with vigorous stirring until orange crystals were formed. The mixture was acidified with dilute acetic acid.The liberated diacid was filtered, washed with waterand dissolved in hot potassium carbonate solution to obtain an orange colored solution. This solution was concentrated to obtain orange crystals of potassium salt of diacid. On acidifying with dilute acetic acid, rose colored 4,4'-azodibenzoic acid (***a***) was obtained. The results are presented in Scheme 1.



Scheme1. Synthesis of 4,4'.azodibenzoic acid

Preparation of PAMAM dendrimer via excess reagent method preparation of ester terminated group ($G_{0.5}$)

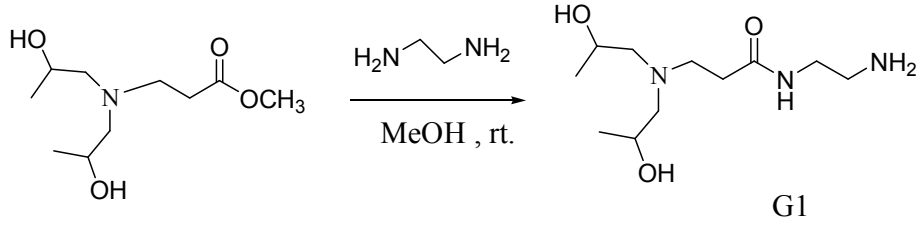
A solution of freshly distilled diisopropanolamine (15 g) in methanol (75 mL) was added dropwise over a period of 1.5h to a stirred solution of methylacrylate (81.2 mL), under nitrogen atmosphere. The mixture stood still at room temperature for 72 h. The solvent was removed under reduced pressure at 75°C using a rotary evaporator and then the resulting light yellow color oil was dried under vacuum (10^{-1} mm Hg, 50°C) to give the pure product (17.23 g, 85%). Synthesis ofPAMAM dendrimer ester terminatedgroup ($G_{0.5}$) was shown in Scheme 2.



Scheme 2. Synthesis ofPAMAM dendrimer ester terminatedgroup($G_{0.5}$)

Preparation of PAMAM dendrimer amine terminated (G_1)

The solid of precursor ($G_{0.5}$) (10g) in methanol (50 mL) was carefully added to a vigorously stirred solution of 1,2-diaminoethane (61.1 mL) at room temperature. Then, the mixture was stirred for 72h at room temperature. The solvent was removed under reduced pressure in 75 °C. PAMAM dendrimer NH_2 end group G_1 precursor is a yellow oil (225.39 g, 88%). G_1 was shown in Scheme 3.

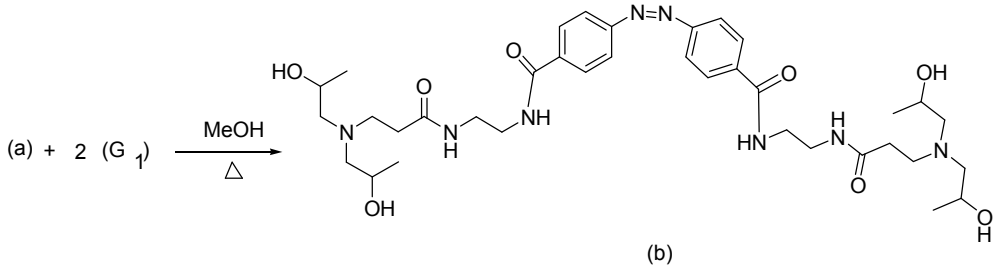


Scheme 3. Synthesis ofPAMAM dendrimers monoamine terminatedgroup (G_1)

Preparation of branched diazobenzene by PAMAM dendrimer (G_1)

The solid of 4,4'-azodibenzoic acid (5g)(a) in methanol (50 mL) which was carefully added to a vigorously stirred solution of PAMAM dendrimer (10g) mono-amine terminatedgroup(G_1) was solved in methanol (75 mL). The mixture was stirred for 14 days

at 37 °C. The solvent was removed under reduced pressure in 75 °C. The branched diazobenzene by PAMAM dendrimer (***b***) precursor as a yellow colour soiled (12.39 g, 82%) was shown in Scheme 4.



Scheme 4. Synthesis of branched diazobenzene by PAMAM dendrimer

Selected spectral data 4,4'-Azodibenzoic acid (*a*):

Rose solid, FT-IR (KBr): 3400cm^{-1} (-OH), 1604 cm^{-1} (streching C=O), 1517 cm^{-1} (-N=N), 850 cm^{-1} (op. Aryl –C=C); ^{1}H-NMR (FT-400 MHz, DMSO):δ; 11(s, 2H), 8.33(d, 4H), 8.14 (d, 4H);^{13}C NMR (400 MHz, DMSO): 122. 91, 130.61, 133.12, 157.93, 169.40; CHN-O: C (62.2%), N (10.35%), H (3.73%) and O (23.72%).

PAMAM dendrimer ester terminated group ($G_{0.5}$):

White yellow solid oil, FT-IR (KBr): 3400cm^{-1} (-OH), 1733 cm^{-1} (streching C=O), 1136 cm^{-1} (streching C-O); ^{1}H NMR (FT-400 MHz, DMSO):δ; 2.44(s, 2H), 1.11(d, 6H), 3.32 (m, 2H), 2.63(d, 4H), 2.73(t, 2H), 2.37 (t, 2H), 3.68(s, 3H);^{13}C NMR(400 MHz, DMSO): 22.21, 34.31, 45.11, 52.20, 63.80, 65.92, 173.11.

PAMAM dendrimer amine terminated (G_1):

Yellow solid oil, FT-IR(KBr): 3300 cm^{-1} (-NH), 1643 cm^{-1} (streching C=O); ^{1}H NMR (FT-400 MHz, DMSO):δ; 2.15(s, 2H), 1.12(d, 6H), 3.63 (m, 2H), 2.53(d, 4H), 2.66(t, 2H), 2.29 (t, 2H), 3.44(t, 2H), 2.98 (t, 2H), 2.62(s, 2H), 8.11(s, H); ^{13}C NMR(400 MHz, DMSO): 22.0, 33.8, 40.5, 42.1, 51.11, 51.8, 63.5, 65.7, 172.20.

Diazobenzene derivative PAMAM dendrimer G_1 (b):

Yellow solid, FT-IR (KBr): 3400cm^{-1} (-OH), 1604 cm^{-1} (streching C=O), 1517 cm^{-1} (-N=N), 850 cm^{-1} (op. Aryl–C=C); ^{1}H-NMR(FT-400 MHz, DMSO):δ; 8.15 (m, 8H), 2.15(s, 4H), 1.21(d, 12H), 2.28 (t, 4H),

2.63(m, 12H), 3.50(m, 8H), 3.62 (m, 4H), 8.10 (s, 4H); ^{13}C NMR (400 MHz, DMSO): 22.0, 33.8, 40.5, 42.1, 51.11, 51.8, 63.5, 65.7, 172.20 122. 91, 130.61, 133.12, 157.93; CHN-O: C (59.3%), N (15.37%), H (7.74%) and O (17.59%).

Results and Discussion

Experimental data have been collected according to this fact that the various generations of PAMAM denderimers and derivative have been synthesized. CHN-O data analysis also showed that the amount of nitrogen has been increased from 10.03% to 15.37% in (**a**) to (**b**) respectively. FT-IR analysis of components and two generations of PAMAM indicated the presence of methoxy groups in $G0._5$ which can be replaced by amino groups in G_1. Data analysis of FT-IR spectra for $G0._5$ is as follows: Functional groups ester(C=O) stretching vibration at1733.3 cm-1 for $G0._5$, have been moved . In this range, C=O amide groups have not been shown. C-O stretching vibration for metoxyin the $G0._5$, has been appeared at 1203.9 cm^{-1}. Data analysis of FT-IR spectra for G_1 demonstrated that C-O stretching vibration for metoxy in G_1 has not been observed . NH at 1556.4 cm^{-1} for G_1 appeared, NH_2 can be seen in 3300-3500 (m) cm^{-1}. C=O starching group ester would not be presented. Infrared spectroscopy analysis for PAMAM NH_2& CO_2Me end groups has been done. FT-IR spectrum in generation one, has been shown a CO (broad) stretching vibration in acid end group at 1024 cm^{-1}. ^{1}H NMR data analysis also confirmed the synthesis of dendrimer and derivative in which hydrogen of metoxy group was appeared at 3.68 ppm in $G0._5$ while hydrogen of amino groups have been at 2.26 ppm for G_1. Through comprehensive characterization of the surface functioned PAMAM dendrimer of G_1, one can have a general profile of the structural characteristics of lower generation PAMAM upon surface substitution. C=O starching carboxylic groups have not been showed at (**b**).The double peak for NH_2 PAMAM G_1 has been removed at azobenzenederivative PAMAM dendrimer (**b**).

Conclusion

4,4'-Azodibenzoic acid (***a***) has been prepared by many different methods. 4,4'-Azodibenzoic acid was prepared according to a typical procedure that was shown in Scheme 1. So, azobenzenederivative PAMAM dendrimerwasprepared according to a typical procedure that was shown in Scheme 4. Moreover, the simplicity of method was also suggested for the synthesis of azobenzenederivative PAMAM dendrimer.

Acknowledgement

The authors are grateful to Payame Noor University for receiving financial support.

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