Polymer Bulletin 49, 1-8 (2002)

Polymer Bulletin

A novel hyperbranched polyester functionalized with azo chromophore: synthesis and photoresponsive properties

Guojie Wang, Xiaogong Wang (✉)

Department of Chemical Engineering, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, P. R. China
Fax: 86-10-62770304, e-mail: wxg-dce@mail.tsinghua.edu.cn

Received: 1 April 2002 /Revised version: 10 July 2002/ Accepted: 15 July 2002

Summary

A hyperbranched polymer containing azo chromophores on the periphery has been synthesized from transesterification reaction between a hyperbranched polyester bearing peripheral hydroxyl groups and ethyl 4-{4'-[*N, N*-di(hydroxyethyl)aminobutoxy]phenylazo}benzoate. The hyperbranched polyester was obtained by adding the AB_2 monomers step by step to a multifunctional core molecule. Narrow molecular weight distribution, with a polydispersity index as low as 1.1, was achieved by this method. The azobenzene- functionalized hyperbranched polymer as well as the corresponding azo monomer showed typical photoresponsive behavior of an azobenzene type molecule. The trans azobenzene units of the hyperbranched polymer could be reversibly switched by UV irradiation to the cis form that recovered slowly to the trans form in the dark. However, significantly less conversion from the trans isomer to the cis isomer was observed for the azobenzene-functionalized hyperbranched polymer at the photostationary states under the irradiation of UV light, which could be attributed to the increased steric hindrance in the hyperbranched polymer.

Introduction

In recent years, hyperbranched polymers have attracted a great deal of attention for their special structure and interesting properties [1-5]. The highly branched architecture leads to globular and void-containing shapes, high solubility, low solution or melting viscosity compared to linear analogues. Azobenzene-functionalized linear polymers have been studied and optimized for a wide range of applications such as liquid crystal displays and devices, reversible optical storage systems, nonlinear optical waveguides, photorefractive switches, and holographic gratings [6-9]. Dendrimers with photoresponsive azobenzene units in the exterior [10-14], interior [15-20], or throughout the dendritic architecture [21-24] have recently been designed and prepared. The incorporation of azo moieties in dendrimers can potentially widen the application of dendrimers in areas such as photoresponsive materials for self-assembly and encapsulation. Although some azo dendrimers have been investigated, to our knowledge, few photoresponsive azobenzene-functionalized hyperbranched polymers have been exploited so far [5]. Here we report a novel photoresponsive azobenzene-functionalized hyperbranched polymer based on a precursor hyperbranched polyester. One main advantage of the methodology reported in this work is that it can produce dentritic azo polymers with structure and properties differing obviously from conventional linear or moderately branched polymers through a relatively simple way. Due to the easy availability, the azobenzene modified hyperbranched polymer could be used in various photonic applications such as photo-switch sensor materials.

Experimental part

*Synthesis of Methyl 3-[*N, N*-di(hydroxyethyl)amino]propionate*

Diethanolamine (0.1 mol) and methylacrylate (0.1 mol) were added to 10 ml of methanol. The mixture was stirred at room temperature for 30 min. Then the temperature of the solution was raised to 35 °C and kept at the temperature for 4 h. After reaction, methanol was removed under high vacuum at room temperature. The product as colorless oil was obtained. ^{1}H NMR ($CDCl_3$): 3.67 (broad, $-CH_2\mathit{OH}$, 2H); $\delta = 3.55$ (s, $-\mathit{CH_3}$, 3H); 3.45 (t, $-\mathit{CH_2}OH$, 4H); 2.73 (t, $-N-\mathit{CH_2}-CH_2-COO-$, 2H); 2.50 (t, $-N-\mathit{CH_2}-CH_2OH$, 4H); 2.37 (t, $-CH_2-COO-$, 2H).

*Polycondensation of Methyl 3-[*N, N*-di(hydroxyethyl)amino]propionate*

1,1,1-trimethylolpropane (TMP, 0.01 mol), Methyl 3-[*N, N*-di(hydroxyethyl)amino]-propionate (0.09 mol) and *p*-toluenesulfonic acid (TSA, 0.09 g) were added into a three-necked flask equipped with a mechanical stirrer, N_2 inlet and reflux condenser. The mixture was stirred at 130 °C for 3 h and then under high vacuum (40 mm Hg) for 1 h. Into the above system, Methyl 3-[*N, N*-di(hydroxyethyl)amino]propionate (0.12 mol) and *p*-toluenesulfonic acid (0.12 g) were added. The mixture was continuously stirring at 130 °C for 3 h and under high vacuum for 1 h. The obtained hyperbranched polyester $\mathbf{P_3}$ was a very sticky liquid with a light yellow color.

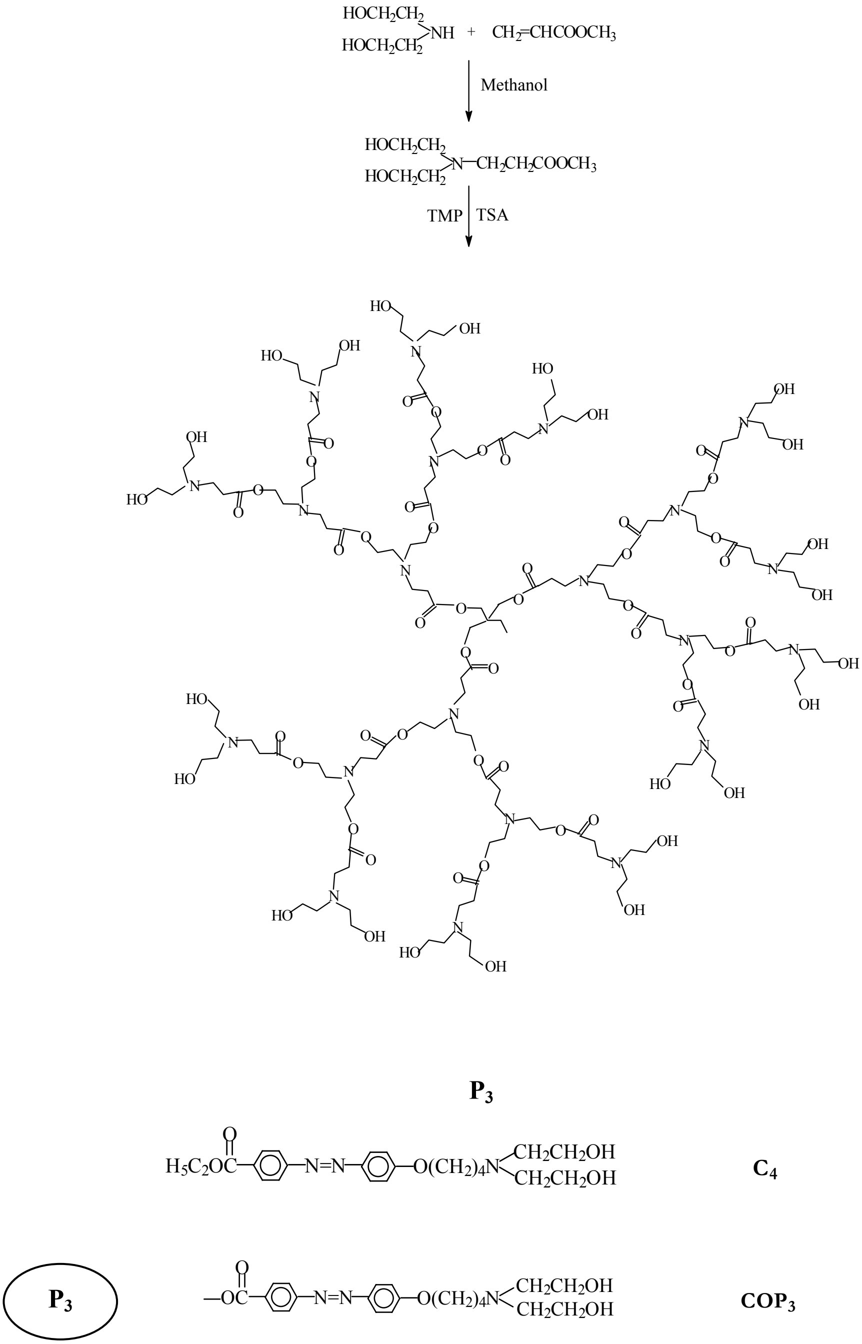
*The synthesis of Ethyl 4-{4'-[*N, N*-di(hydroxyethyl)aminobutoxy]phenylazo} benzoate* $\mathbf{C_4}$ *has been described elsewhere [5].*

Synthesis of the azobenzene-functionalized hyperbranched polyester $\mathbf{COP_3}$

$\mathbf{P_3}$ (5.0 g), $\mathbf{C_4}$ (0.3 g) and *p*-toluenesulfonic acid (0.02 g) were mixed in a three-necked flask equipped with a mechanical stirrer, N_2 inlet and reflux condenser. The mixture was stirred at 130°C for 3 h and then under high vacuum for 1 h.

Characterization

^{1}H NMR spectra were recorded on a Bruker AM-200 MHz FT-NMR spectrometer. UV-Vis spectra were measured with a Perking Elmer Lambda Bio-40 spectrometer. The molecular weight of the hyperbranched polymer was determined by gel permeation chromatography (PL–GPC210) with styragel columns relative to polystyrene standards and using tetrahydrofuran (THF) as eluent.



Scheme 1. Chemical structure of $\mathbf{P_3}$, $\mathbf{C_4}$ and azobenzene-functionalized hyperbranched polymer $\mathbf{COP_3}$

Results and discussion

Synthesis

Hyperbranched polymers are usually prepared by one-step polymerization resulting in highly branched but less regular structures comparing to dendrimers. Continuous, slow addition of AB_2 monomer to a multifunctional core can result in high molecular weight hyperbranced polymers with narrow polydispersities [25]. In this work, a core molecule was introduced and the reaction was controlled through a step-by-step addition process in order to obtain a hyperbranched polymer with more regular structure. 1,1,1-trimethylolpropane was used as the core molecule. Methyl 3-[*N, N*-di(hydroxyethyl)amino]propionate was used as the AB_2 monomer, which was synthesized via Michael addition of methyl acrylate and diethanolamine. The synthetic procedure was a transesterification reaction performed in the bulk using an acid catalyst and involved no purification steps before further reaction. A vigorous stir was used to overcome the increasing viscosity of the polymer/monomer mixture. The polyester became stickier and sticker with the increase of the reaction time and the amount of monomer. The hyperbranched polyester P_3 was characterized by GPC using THF as eluent (Mn=707, Mw/Mn=1.06). The experimentally determined Mn value estimated by comparison with polystyrene standards differed pronouncedly from the theoretical value (3473). As the relationship between molar mass and hydrodynamic radius for a hyperbranched polymer differs from that of its linear counterpart with the same molar mass, its molecular weight determined by GPC could be smaller than the real value [26]. The polydispersity index indicated a narrow distribution of hydrodynamic radius. The ideal molecular structure of the polyester is shown in Scheme 1. The ^1H NMR spectrum of the polyester is given in Figure 1. The broad peaks in the spectrum are caused by the hyperbranched structure.

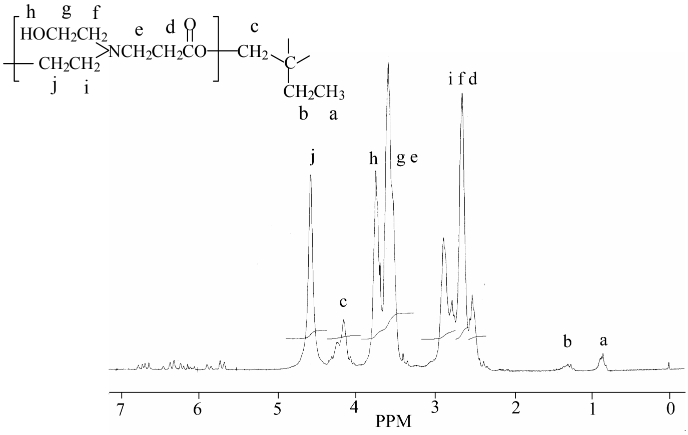


Fig. 1. ^1H NMR spectrum of $\mathbf{P_3}$ in $CDCl_3$.

Ethyl 4-{4'-[*N, N*-di(hydroxyethyl)aminobutoxy]phenylazo}benzoate $\mathbf{C_4}$, a functional molecule containing azo chromophore, was prepared by the reaction of ethyl 4-[4'-(1-bromobutoxy)phenylazo]benzoate with diethanolamine in ethanol, recrystallized from acetonitrile with 80% yield. Its structure is shown in Scheme 1.

Photoresponsive azobenzene-functionalized hyperbranched polymer **COP_3** was obtained by modification of the polyester P_3 with azobenzene molecule **C_4**. The hydroxyl groups in periphery of **P_3** reacted with **C_4** by eliminating ethanol through transesterification reaction. In order to avoid the reaction between **C_4** molecules, the modification of **P_3** was carried out with a limited amount of **C_4**. Under this condition, azobenzene chromophores should be mainly incorporated in the periphery of the hyperbranched polyester. The structure of **COP_3** is shown in Scheme 1 and its ^1H NMR spectrum is shown in Figure 2. The molecular weight of the polymer **COP_3** was determined to be Mn=752 (Mw/Mn=1.03) by GPC using THF as eluent, which was smaller than its theoretical value for its hyperbranched structure. The determined Mn of **COP_3** by GPC was bigger than that of **P_3**, for **COP_3** was prepared from **P_3** and **C_4**.

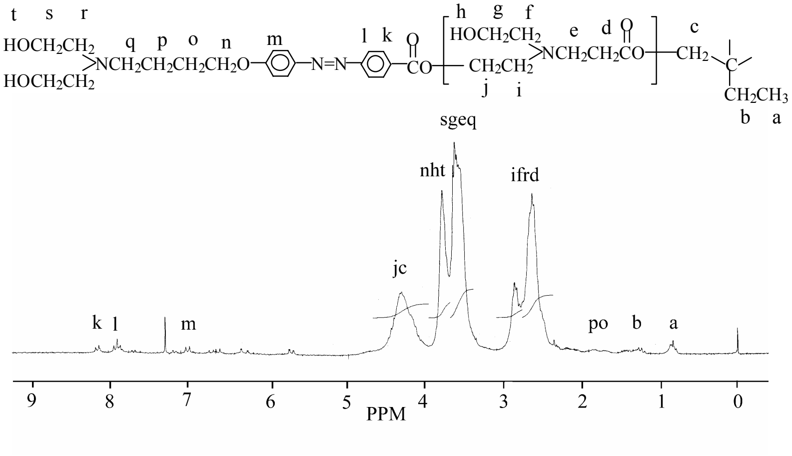
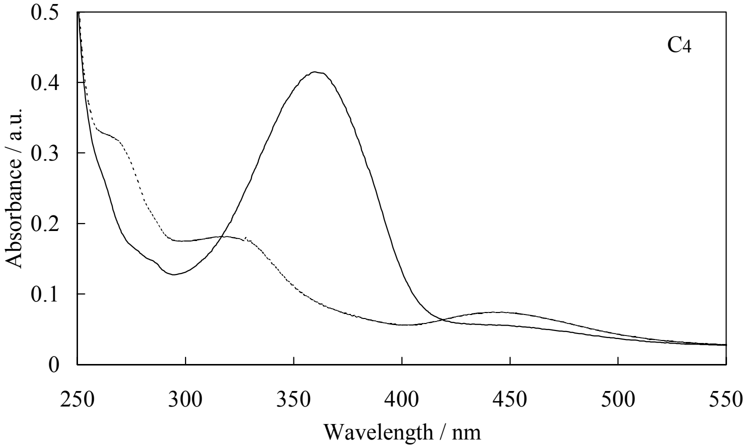


Fig. 2. ^1H NMR spectrum of **COP_3** in $CDCl_3$.

Photoresponsive properties

The azo compounds and azo polymer synthesized in this work exhibited a typical spectral variation of azobenzene type chromophores resulted from the trans-to-cis photoisomerization and cis-to-trans thermal isomerization. The experiments were carried out in chloroform at 300 K. The changes in the UV-Vis absorption spectra of the compound **C_4** and the azobenzene-functionalized hyperbranched polymer **COP_3** in $CHCl_3$ upon irradiation at 365 nm are shown in Figure 3. The compound **C_4** and the azobenzene-functionalized polymer exhibit their absorption maxima at about 358 nm and week bands at about 444 nm which are related to π-π^* and n-π^* transition bands of the trans azobenzene, respectively. Upon UV irradiation, the intensity of π-π^* transition band at 358 nm decreased and intensity of n-π^* transition band at 444 nm increased gradually. The photostationary states were obtained after irradiating for about 20 seconds. Standing in the dark, the contents of trans azobenzenes of **C_4** and **COP_3** recovered completely in 30 h.



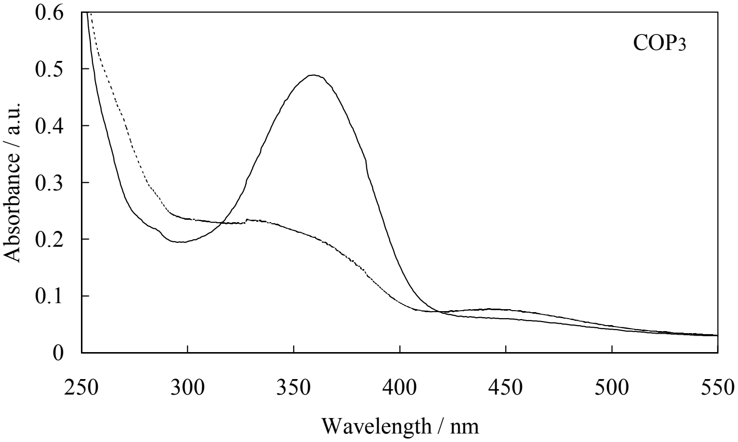


Fig. 3. The absorption spectra of $\mathbf{C_4}$ and azobenzene-functionalized hyperbranched polymer $\mathbf{COP_3}$ in $CHCl_3$ before UV irradiation (solid line) and at the photostationary states after UV irradiation (dot line).

The cis isomer fraction Y [27] was determined from the absorbances by

$$Y = 1.05\times(1 - A/A_{dark})$$

where A_{dark} = peak initial absorbance with only trans isomer present at 358 nm and A = absorbance at 358 nm at the photostationary state. Irradiation of UV light yielded equilibrium with 67% cis isomer in azobenzene-functionalized polymer $\mathbf{COP_3}$. The compound $\mathbf{C_4}$ exhibited the similar changes in the absorption spectrum, while the percentage of cis isomer observed in the photostationary state was 91%. Although the different photoconversion rates of azo chromophores in different states such as rubbery and glassy states has been reported [28], the difference in the cis content at the photostationary state between azobenzene-containing hyperbranched polymers and their monomers in their solutions has scarcely been reported. Compared to the compound **C_4**, the hyperbranched polymer showed less conversion from the trans isomer to cis isomer at the photostationary states, which was attributed to the increased steric hindrance in the hyperbranched polymer. This observation could be explained as evidence that the branches at the periphery could reenter and be involved in the inner part of the hyperbranched structures in some extent.

Conclusion

A narrow polydispersed hyperbranched polyester **P_3** with peripheral hydroxyl groups was synthesized through a step by step addition process by using 1,1,1-trimethylolpropane as a core molecule and Methyl 3-[*N, N*-di(hydroxyethyl)amino]propionate as an AB_2 monomer. Ethyl 4-{4'-[*N, N*-di(hydroxyethyl)aminobutoxy]phenylazo}benzoate **C_4** was reacted with **P_3** to obtain photoresponsive azobenzene-functionalized hyperbranched polymer **COP_3**. Both **C_4** and **COP_3** exhibit a typical spectral variation of azobenzene type chromophores resulted from the trans-to-cis photoisomerization and cis-to-trans thermal isomerization. However, significant difference between the percentages of cis isomers in the photostationary state for **C_4** (91%) and **COP_3** (67%) was observed. The less conversion from trans isomer to cis isomer at the photostationary for the azobenzene-functionalized hyperbranched polymer is due to the increased steric hindrance surrounding the azo chromophores. The synthesized hyperbranched polyesters **P_3** and **COP_3** possess a good ability to dissolve in water owing to the tertiary amine in the structure and they can be used as polycation to fabricate self-assembled film, as will be reported later.

Acknowledgements: The authors are grateful to the National Natural Science Foundation for the financial support under Project 59925309 and the Postdoctoral Science Foundation of China.

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