Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

Synthesis and Characterization of Azobenzene-Functionalized Hyperbranched Polymers

MD. Zahangir Alam[a]; Tomonari Ogata[a]; Yutaka Kuwahara[a]; Seiji Kurihara[a]
[a] Faculty of Engineering, Department of Applied Chemistry and Biochemistry, Kumamoto University, Kumamoto, Japan

First published on: 11 November 2010

To cite this Article Alam, MD. Zahangir , Ogata, Tomonari , Kuwahara, Yutaka and Kurihara, Seiji(2010) 'Synthesis and Characterization of Azobenzene-Functionalized Hyperbranched Polymers', Molecular Crystals and Liquid Crystals, 529: 1, 25 — 31
To link to this Article: DOI: 10.1080/15421406.2010.495658
URL: http://dx.doi.org/10.1080/15421406.2010.495658

Mol. Cryst. Liq. Cryst., Vol. 529: pp. 25–31, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.495658

Taylor & Francis
Taylor & Francis Group

Synthesis and Characterization of Azobenzene-Functionalized Hyperbranched Polymers

MD. ZAHANGIR ALAM, TOMONARI OGATA, YUTAKA KUWAHARA, AND SEIJI KURIHARA

Faculty of Engineering, Department of Applied Chemistry and Biochemistry, Kumamoto University, Kumamoto, Japan

Azobenzene functionalized hyperbranched polymers (HBAzPs) have been synthesized by polycondensation of 4,4′-di((2-hydroxyethoxy)azobenzene and 1,3,5-benzenetricarboxylic acid chloride in presence of triethylamine at room temperature through $A_2 + B_3$ polymerization approach. The structure and properties of HBAzPs were characterized by ^1H NMR, IR, GPC, DSC and UV-Visible spectrometry. Molecular weights as well as properties of HBAzPs were found to be greatly influenced by molar ratio of monomers, amount of triethylamine and monomer concentration. HBAzP solutions in THF showed absorbances at 356 nm and 450 nm corresponding to π-π^* and n-π^* electronic transitions of azobenzene chromophores, respectively. A reversible trans-cis photoisomerization of HBAzPs was observed upon irradiation of UV and visible light.

Keywords $A_2 + B_3$ polymerization; hyperbranched azopolymer; *trans-cis* photoisomerization

Introduction

Hyperbranched polymers (HBPs) are highly branched macromolecules with three-dimensional architecture. Because of their structural characteristics HBPs show many interesting properties of the dendritic polymers such as good solubility, low melting viscosity, and large amount of terminal functional groups. Dendrimers have a well-controlled size and shape, and are prepared by tedious multistep reactions through a divergent or convergent scheme whereas HBPs can be synthesized very easily by a simple one-pot synthetic procedure. Thus HBPs offer a good alternative to the more perfect dendrimers. That's why recently a great deal of attention was devoted to HBPs [1–5].

Address correspondence to Seiji Kurihara, Faculty of Engineering, Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kumamoto-si, Kumamoto 860-8555, Japan. Tel.: +81-96-342-3678; Fax: 81-96-342-2679; E-mail: kurihara@gpo.kumamoto-u.ac.jp

Introducing azobenzene-chromophore can significantly modify the properties of HBPs. Azobenzene molecules exist in two isomeric states: *trans*-form which are rod-shaped and *cis*-form which possess a bent shape. It is well known that a reversible *trans-cis* photoisomerization can be observed by irradiation of UV and visible light respectively. The bent structure causes a large effect on molecular arrangements of azobenezene molecules. The two states of azobenzene molecules have distinct absorption spectra which allow reversible storage of data. 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]. Recently hyperbranched polymers functionalized with azobenzene chromophores have been designed and prepared from AB_2 monomers [10–12]. But, HBPs prepared by one-step polycondensation of AB_2 type monomers possess highly irregular structures and large molecular weight distributions [13,14]. In this study we were envisioned to synthesize HBAzPs through $A_2 + B_3$ polymerization approach as a lot of monomers are commercially available.

Experimental

An A_2 type monomer 4,4′-di(2-hydroxyethoxy)azobenzene (DH2Az) was synthesized in good yield and purity. Hyperbranched azopolymers were synthesized by condensation polymerization of DH2Az and trimesoyl chloride (TMC) in presence of triethylamine (TEA) as basic catalyst in dioxane (DO) at room temperature through $A_2 + B_3$ polymerization approach. Gel permeation chromatography (GPC) analyses using tetrahydrofuran (THF) as eluent revealed molecular weights and polydispersity indexes of HBAzPs. ^{1}H NMR and IR spectroscopy were also used for characterization of HBAzPs. Differential Scanning Calorimetry (DSC) experiments were performed on a Seiko SSC-5020 instrument at a temperature rate of 10°C per minute. Polarizing optical microscopy (POM) observations were made with Olympus BHSP polarizing microscope equipped with a Mettler FP 80 hot stage controlled by Mettler unit. The heating and cooling cycles were performed at a rate of $10^{\circ}C\,min^{-1}$. Reversible *tran-cis* photoisomerization behaviors of HBAzPs were studied upon irradiation of UV (366 nm) and visible light (436 nm), respectively.

Synthesis of 4,4′-di(2-hydroxyethoxy)azobenzene, DH2Az

Synthesis of 4,4′-dihydroxyazobenzene (DHAz). 20.0 g (181 mmol) of *p*-aminophenol was dissolved in 200 ml of 1 M HCl solution and was cooled to 0°C in an ice bath. 12.6 g (181 mmol) of $NaNO_2$ dissolved in 300 ml of water was added dropwise to solution of *p*-aminophenol at 0°C. 400 ml of pre-cooled methanol was added to this diazotized solution and the solution was added drop-wise to 17.1 g (181 mmol) of phenol dissolved in 120 ml 3 M aqueous potassium hydroxide solution. This solution was stirred at room temperature for 2 h. Then methanol was removed from the reaction mass by evaporation and was acidified with aqueous HCl up to a pH value of 4.0. The resulting precipitate was collected by filtration and washed with water until neutralization. The crude DHAz was purified by recrystallization from ethanol/water mixture and dried under vacuum. Yield: 56.1%, melting point: 218°C.

Synthesis of 4,4′-di(2-hydroxyethoxy)azobenzene, DH2Az

4,4′-Dihydroxyazobenzene 20.0 g (90.5 mmol), potassium carbonate 25.0 g (181 mmol), 2-chloroethanol 15.3 g (181 mmol) and a small amount of potassium iodide was dissolved in 500 ml DMF in a flask and the reaction mass was stirred at 100°C for 48 h. After the reaction time is over the reaction mass was poured into a large amount of water and precipitate was collected by filtration. The crude DH2Az was purified by recrystallization from ethyl acetate and dried under vacuum. Yield: 24.0%, Melting point: 198°C. Anal.: Calcd. (%); H; 6.00, C; 63.56, N; 9.27. Found: (%); H; 5.95, C; 63.75, N; 8.89.

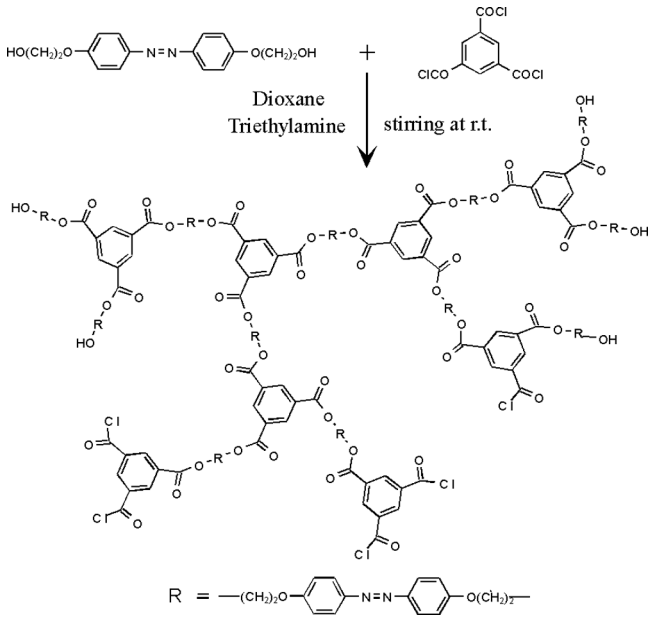
Synthesis of HBAzPs

Required amounts of DH2Az and TMC dissolved in dioxane were taken in a flask equipped with a stirrer, gas-inlet and gas-outlet tubes. Nitrogen gas was passed through the polymerization solution for about one hour. TEA dissolved in dioxane was added slowly to $A_2 + B_3$ polymerization solution with a dropping funnel. After addition of TEA the polymerization solution was stirred at room temperature under nitrogen for the desired period. Then the polymerization solution was poured into methanol to obtain the precipitate of HBAzPs. The precipitated polymer was filtered off and was purified by $CHCl_3$/methanol reprecipitation technique, and dried under vacuum at room temperature.

Results and Discussions

HBAzPs were synthesized by condensation polymerization of DH2Az and TMC in presence of TEA at room temperature through $A_2 + B_3$ polymerization approach. The synthetic route, structure of monomers and HBAzPs are shown in Scheme 1. All polycondensation reactions were carried out at room temperature due to very high reactivity of TMC. Molar ratio and concentration of monomers, amount of TEA and polymerization time were varied to explore their effects on $A_2 + B_3$ polymerization. In this study polymerizations were carried out with monomer ratios of A_2:$B_3 = 3{:}2$ and 1:1 corresponding to stoichiometric amount and excess of B functionalities, respectively. Table 1 shows the polymerization conditions and characterization of the resultant HBAzPs. It is observed that monomer ratio has a crucial influence on the properties of HBAzPs. With stoichiometric monomer ratio and little excess of TMC monomer higher molecular weight HBAzPs were obtained. But, possibility of gelation was also higher. Gelation can be avoided only by optimization of polymerization conditions. Apparent molecular weights of HBAzPs determined by GPC using polystyrene as standard were found to be relatively low. But the actual molecular weights are supposed to be three to five times higher than the obtained value since highly branched polymers are known to have smaller hydrodynamic volume than their linear analogues [15–17].

The data in Table 1 also reveal the effect of monomer concentration and time on molecular weights of HBAzPs. Molecular weights of HBAzPs were found to be increased with an increase in monomer concentration. But the possibility of gelation is higher in case of concentrated polymerization solution. Molecular weights of HBAZPs increased a little with an increase in polymerization time. In the polycondensation of DH2Az and TMC, a relatively fast reaction occurred at the beginning



Scheme 1. Synthesis of HBAzPs through $A_2 + B_3$ polymerization approach.

compared to the subsequent propagation. So, polymerization time exhibited a little effect on molecular weight of HBAzPs.

TEA which is a basic catalyst in nature was used as condensing agent in this $A_2 + B_3$ polymerization. A significant effect of TEA on molecular weight of HBAzPs was observed. Molecular weights of HBAzPs were found to increase with an increase in the amount of TEA. It is assumed that TEA enhanced polycondensation reactions. But, gelation was found to be occurred in case of using an excess amont of TEA. In the synthesis of HBAzPs gelation can be avoided by optimizing the reaction conditions.

Figure 1 shows the IR spectra of monomers (i) DH2Az, (ii) TMC and (iii) HBAzP-I. Monomer DH2Az exhibited –OH group characteristic absorption peak at 3,290 cm^{-1}. In the IR spectra of TMC the absorption peak corresponding to

Table 1. Polymerization conditions and characterization of HBAzPs

HBAzPs	BAz20H mmol	TMC mmol	TEA mmol	DO ml	Time h	Mw	Mw/Mn
HBAzP I	1.00	0.75	2.0	10	24	3900	1.53
HBAzP II	1.00	0.67	2.0	20	6	2500	1.30
HBAzP III	1.00	0.67	2.0	50	14	2200	1.50
HBAzP IV	0.50	0.37	1.25	20	24	2900	1.23
HBAzP V	0.50	0.37	2.0	20	Gel		
HBAzP VI	0.50	0.50	1.0	20	24	3000	1.30
HBAzP VII	0.50	0.50	1.0	30	24	2400	1.32

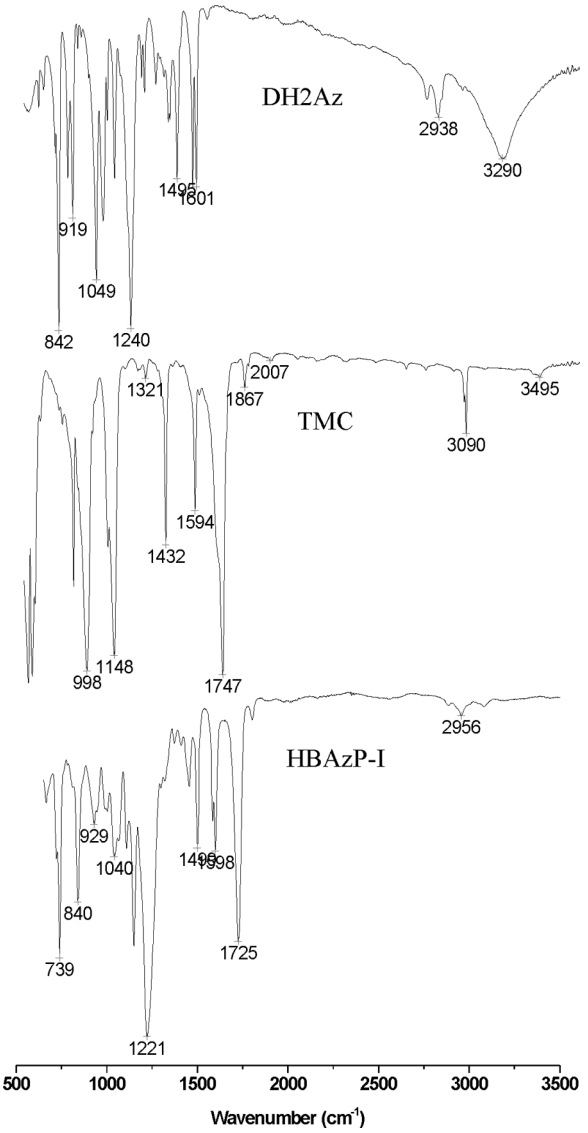


Figure 1. IR-spectra of DH2Az, TMC and HBAzP-I.

carbonyl (C=O) group was observed at 1747 cm^{-1} while this peak in the HBAzP-I spectra is shifted to shorter wavelength (1725 cm^{-1}) due to the formation of ester. The absorption peaks corresponding to the azobenzene chromophore of monomer DH2Az and HBAzP-I were observed at 1601 and 1598 cm^{-1}, respectively. The absorption peak at 3290 cm^{-1} corresponding to –OH was fully disappeared in the IR spectra HBAzP-I. These data reveal the successful formation of HBAzPs through $A_2 + B_3$ polymerization approach. ^{1}H NMR spectra of DH2Az, TMC and HBAzPs also confirmed the formation of HBAzPs. But, it was not possible to determine degree of branching of HBAzPs with ^{1}H NMR spectra due to the difficulty of assigning dendritic, linear and terminal units accurately.

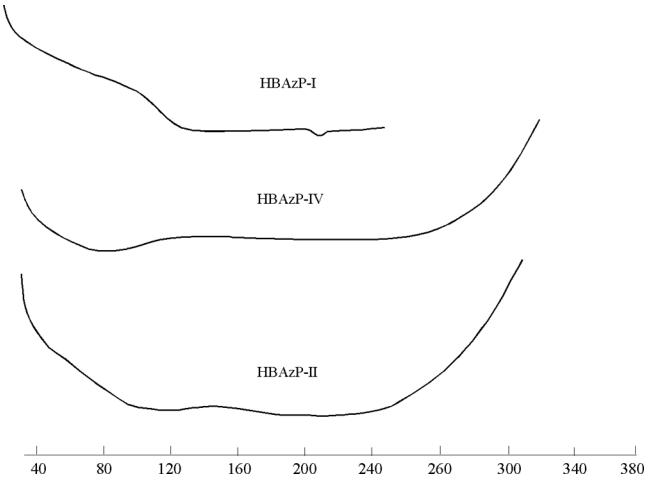


Figure 2. DSC thermograms of HBAzP-I, HBAzP-II and HBAzP-IV.

Thermal properties of HBAzPs were determined by DSC and POM. Only HBAzP-I showed a glass transition at 115°C and isotropization temperature at 210°C. Other HBAzPs mentioned in Table 1 did not show any glass transition temperature. Other HBAzPs exhibited their thermal stability up to about 300°C and decomposed above this temperature. It is assumed that because of the structural rigidity HBAzPs showed excellent morphological stability, with no glass transition temperature detectable in the measured temperature region of the DSC analysis.

HBAzPs synthesized in this study exhibited a typical reversible *trans-cis* photoisomerization. Figure 3 showed the changes in UV-visible absorption spectra of HBAzP-I in THF upon irradiation of (A) UV and (B) visible light. The UV-visible absorption spectra of HBAZP-I in THF showed a strong absorption at 356 nm and a weak absorption at 450 nm corresponding to π-π^* and n- π^* transition of *trans*-azobenzene moiety, respectively. Upon UV light irradiation the intensity of π-π^*

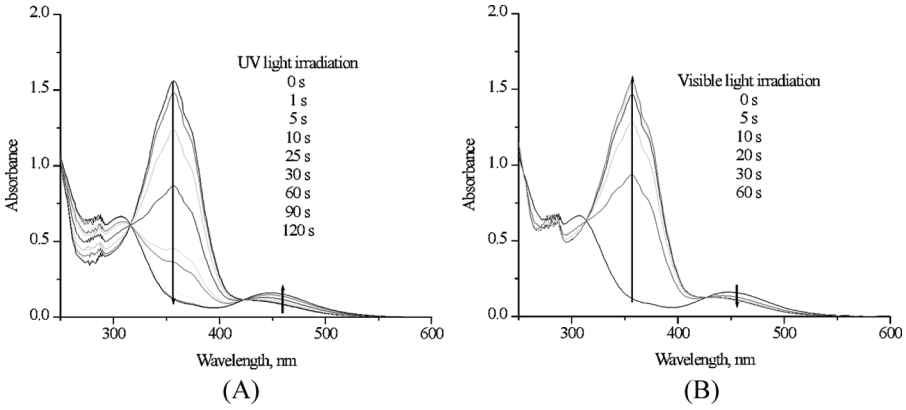


Figure 3. Changes in absorption spectra of HBAzP-I solution in THF by (A) UV and (B) visible light irradiation.

transition band at 356 nm decreased and intensity of n-π^* transition band at 450 nm gradually increased due to *trans–cis* photoisomerization. The photostationary state was observed after an irradiation of 20s. The reversibility of *cis-trans* photoisomerization was confirmed by irradiation of visible light. The UV spectra recorded at different irradiation time were characterized by the presence of two isosbestic points at about 283 and 392 nm, respectively. This reveals that only two absorbing species, namely *cis* and *trans* isomers of azobenzene group are present in the solution.

Conclusion

HBAzPs were successfully synthesized by polycondensation of 4,4′-di(2-hydroxyethoxy)azobenzene and 1,3,5-benzenetricarboxylic acid chloride in presence of triethylamine at room temperature through $A_2 + B_3$ polymerization approach. Molar ratio of monomers, monomer concentration and amount of TEA showed a significant influence on properties of HBAzPs while polymerization time exhibited a very little effect. HBAzPs showed excellent morphological stability due to their structural rigidity. They showed reversible *trans-cis* photoisomerization by irradiation of UV and visible light, respectively. Thus the resulting HBAzPs are expected to find their applications in various photonic devices.

Acknowledgments

The financial support from the Japan Society for the Promotion of Science (No. 08045) to carry out this research is gratefully acknowledged.

References

[1] Jikei, M., & Kakimoto, M. (2001). *Prog. Polym. Sci.*, *26*, 1233.
[2] Inoue, K. (2000). *Prog. Polym. Sci.*, *25*, 453.
[3] Voit, B. (2000). *J. Polym. Sci. A: Polym. Chem.*, *38*, 2505.
[4] Matthews, O. A., Shipway, A. N., & Stoddart, J. F. (1998). *Prog. Polym. Sci.*, *23*, 1.
[5] Wang, G. J., Cheng, H., & Wang, X. G. (2002). *Chem. Lett.*, *31*, 78.
[6] Wang, X. G., Balasubramanian, S., Li, L., Jiang, X. L., Sandman, D. J., Rubner, M. F., Kumar, J., & Tripathy, S. K. (1997). *Macromol. Rapid Commun.*, *18*, 451.
[7] Oge, T., & Zentel, R. (1996). *Macromol. Chem. Phys.*, *197*, 1805.
[8] Ikeda, T., & Tsutsumi, O. (1995). *Science*, *268*, 1873.
[9] Xie, S., Natansohn, A., & Rochon, P. (1993). *Chem. Mater.*, *5*, 403.
[10] Wang, G. J., & Wang, X. G. (2002). *Polym. Bull.*, *49*, 1.
[11] Brenner, A. R., & Voit, B. I. (1996). *Macromol. Chem. Phys.*, *197*, 2673.
[12] Jin, M., Lu, R., Bao, C. Y., Xu, T. H., & Zhao, Y. Y. (2004). *Polymer*, *45*, 1125.
[13] Bharathi, P., & Moore, J. S. (2000). *Macromolecules*, *33*, 3212.
[14] Mock, A., Burgath, A., Hanselmann, R., & Frey, H. J. (2001). *Macromolecules*, *34*, 7692.
[15] Lim, Y., Kim, S., Lee, Y., Lee, W., Yang, T., Lee, M., Suh, H., & Park, J. (2001). *J. Am. Chem. Soc.*, *123*, 2460.
[16] Hawker, C. J., Malmstrom, E., Frank, C. W., & Kampf, J. P. (1997). *J. Am. Chem. Soc.*, *119*, 9903.
[17] Claesson, H., Malmstrom, E., Johansson, M., & Hult, A. (2002). *Polymer*, *43*, 3511.