Synthesis and Properties of a Photoresponsive Azobenzene-Containing Hyperbranched Polymer

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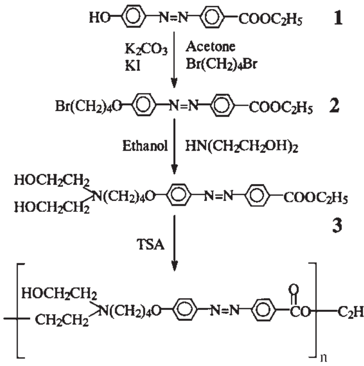
A hyperbranched polymer containing azobenzene chromophores has been synthesized and characterized. The photoresponsive properties of the hyperbranched azo polymer have been studied and compared with those of the monomers.

Azobenzene-containing 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.[1] Nonlinear polymers such as dendrimers with photoresponsive azobenzene units in the exterior,[2] interior,[3] or throughout the dendritic architecture[4] have recently been designed and prepared. Dendritic polymers including dendrimers and hyperbranched polymers are a relatively new class of macromolecules.[5] The highly branched structures lead to their globular, void-containing shapes, high solubility, low solution or melt viscosity compared to linear analogues. Dendrimers have monodisperse structure, while the hyperbranched polymers exhibit a broad molar mass distribution and less regularly branched structure. In many cases, the hyperbranched polymers are discussed as a more rapidly prepared and more economical replacement of perfect dendrimers in various applications. The incorporation of azo moieties in hyperbranched polymers could significantly widen the potential applications of azo dendrimers due to the easier preparation of the former. Although a few photoresponsive azo dendrimers have been investigated, to our knowledge, no photoresponsive hyperbranched polymer has been exploited so far. In this communication, we report the synthesis and properties of a photoresponsive azobenzene-containing hyperbranched polymer. 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 hyperbranched azo polymers could be used in various photonic applications such as photo-switch, photo-storage materials among others.

The polymer was synthesized through a route showed in Scheme 1. The starting compound is ethyl 4-(4′-hydroxyphenylazo)benzoate **1**, prepared by azo coupling reaction between phenol and ethyl 4-aminobenzoate (^{1}H NMR, DMSO, $\delta = 10.50$ 1H, 8.13 2H, 7.92 4H, 7.02 2H, 4.37 2H, 1.35 3H, MP 163 °C). Compound **2** was obtained by the reaction of **1** with an excessive amount of 1,4-dibromobutane in the presence of anhydrous K_2CO_3 and KI in dry acetone with 85% yield (^{1}H NMR, DMSO, $\delta = 8.12$ 2H, 7.92 4H, 7.14 2H, 4.35 2H, 4.13 2H, 3.59 2H, 1.88 4H, 1.34 3H, MP 96 °C). Compound **3** was prepared by the reaction of **2** with diethanolamine in ethanol, recrystallized from acetonitrile with 80% yield (^{1}H NMR, DMSO, $\delta = 8.15$ 2H, 7.93 4H, 7.15 2H, 4.36 2H, 4.11 2H, 3.44 2H, 2.53 6H, 1.76 2H, 1.55 2H, 1.34 3H, MP 115 °C). Compound **3** could keep a good stability when the temperature was below 200 °C as determined by thermogravimetric analysis. The ester exchange reaction of compound **3** was accomplished with *p*-toluenesulfonic acid (5% mole of compound 3) at 130 °C to give the hyperbranched polymer **4** (80% yield). Its ^{1}H NMR spectrum is shown in Figure 1. The chemical shifts and relative intensity of the NMR resonances agree with the structure shown in Scheme 1. The number average molecular weight of polymer **4** was estimated by gel permeation chromatography (GPC) to be with a polydispersity index of 1.5 (Mw = 4354). It has been reported the molecular weights of dentritic polymers measured by GPC are lower than the true values due to the globular shapes.[5]



Hyperbranched polymer **4**

Scheme 1.

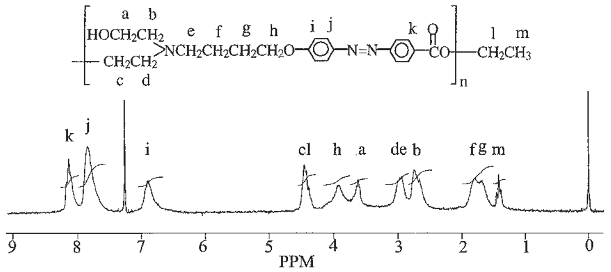


Figure 1. ^{1}H NMR spectrum of hyperbranched polymer **4** in $CDCl_3$.

All the azobenzene compounds and polymers synthesized in this work exhibited a typical spectral variation of azobenzene 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 monomer **3** and the hyperbranched azo polymer **4** in $CHCl_3$ upon irradiation at 365 nm are shown in Figure 2. The monomer **3** and polymer **4** exhibit their absorption maxima at about 358 nm and week band 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 state was obtained after irradiating for 20 seconds. Standing in dark, the contents of *trans* azobenzenes of all compounds and the polymer were recovered completely in 27 hours.

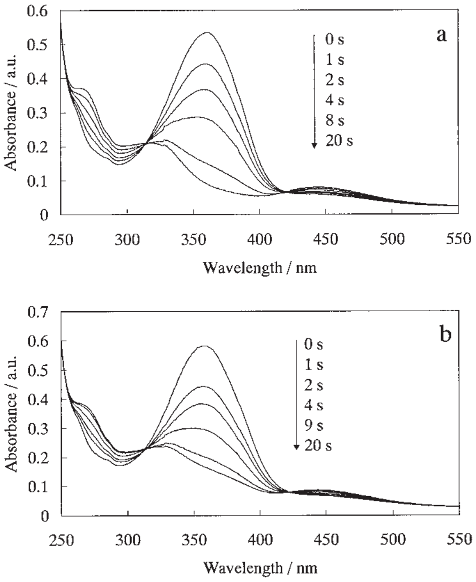


Figure 2. Changes in the absorption spectra of monomer **3** (a) and hyperbranched polymer **4** (b) in $CHCl_3$ upon irradiation at 365 nm in different time.

The *cis* isomer fraction Y^6 was determined from the absorbances by

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

where A_{dark} = peak initial absorbance with only trans isomer present at 358 nm and A = absorbance at 358 nm in the photostatonary state. Irradiation of UV light yields equilibrium with 78% *cis* isomer in polymer **4**. The compound **3** exhibited the similar changes in the absorption spectrum, while the percentage of *cis* isomer in the photostationary state was 91%. Compared to the monomer **3**, hyperbranched polymer **4** shows less conversion from the *trans* isomer to *cis* isomer at the photostationary states, which is attributed to increased steric hindrance in the core of the hyperbranched polymer. Based on this understanding, it is possible to design various types of hyperbranched azo polymers with different photoresponsive extent and rates by smartly exploiting the architecture in the polymers.

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References

1 a) T. Oge and R. Zentel, *Macromol. Chem. Phys.*, **197**, 1805 (1996). b) T. Ikeda and O. Tsutsumi, *Science*, **268**, 1873 (1995). c) B. L. Feringa, W. F. Jager, and B. de Lange, *Tetrahedron*, **49**, 8267 (1993). d) S. Xie, A. Natansohn, and P. Rochon, *Chem. Mater.*, **5**, 403 (1993).

2 a) A. Archut, F. Vogtle, L. De Cola, G. C. Azzellini, V. Balzani, P. S. Ramanujam, and R. H. Berg, *Chem. Eur. J.*, **4**, 699 (1998). b) A. Archut, G. C. Azzellini, V. Balzani, L. De Cola, and F. Vogtle, *J. Am. Chem. Soc.*, **120**, 12187 (1998). c) H. B. Mekelburger, K. Rissanen, and F. Vogtle, *Chem. Ber.*, **126**, 1161 (1993). d) A. P. H. Schenning, C. Elissen-Roman, J. W. Weener, M. W. P. L. Baars, S. J. van der Gaast, and E. W. Meijer, *J. Am. Chem. Soc.*, **120**, 8199 (1998). e) J. W. Weener and E. W. Meijer, *Adv. Mater.*, **12**, 741 (2000).

3 a) D. M. Junge and D. V. McGrath, *Chem. Commun.*, **1997**, 857. b) D. M. Junge and D. V. McGrath, *J. Am. Chem. Soc.*, **121**, 4912 (1999). c) D. L. Jiang and T. Aida, *Nature*, **388**, 454 (1997). d) L. Liao and D. V. McGrath, *Polym. Prep.*, **41**(1), 870 (2000). e) A. Sidorenko, C. Houphouet-Boigny, O. Vilavicencio, M. Hashemzadeh, D. V. McGrath, and V. V. Tsukruk, *Langmuir*, **16**, 10569 (2000). f) S. Ghosh and A. K. Banthia. *Tetrahedron Lett.*, **42**, 501 (2001).

4 a) T. Nagasaki, S. Tamagaki, and K. Ogino, *Chem. Lett.*, **1997**, 717. b) S. Yokoyama, T. Nakahama, A. Otomo, and S. Mashiko, *Chem. Lett.*, **1997**, 1137. c) S. Yokoyama, T. Nakahama, A. Otomo, and S. Mashiko, *J. Am. Chem. Soc.*, **122**, 3174 (2000).

5 a) O. A. Matthews, A. N. Shipway, and J. F. Stoddart, *Prog. Polym. Sci.*, **23**, 1 (1998). b) V. Brigitte, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 2505 (2000).

6 J. G. Victor and J. M. Torkelson, *Macromolecules*, **20**, 2241 (1987).