Hyperbranched Photo Responsive and Liquid Crystalline Azo-Siloxane Polymers Synthesized by Click Chemistry

Someshwarnath Pandey, Sarada P. Mishra, Balakrishna Kolli, Tapan Kanai, Asit B. Samui

Polymer Science and Technology Centre, Naval Materials Research Laboratory, Shil-Badlapur Road, Ambernath 421506, Maharashtra, India

Correspondence to: A. B. Samui (E-mail: absamui@gmail.com)

Received 14 February 2012; accepted 8 March 2012; published online 30 March 2012 DOI: 10.1002/pola.26042

ABSTRACT: Three new types of hyperbranched photoactive liquid crystalline siloxane polymers containing azo moieties were synthesized using click chemistry methodology. The polymers were soluble in most of the polar solvents like chloroform, tetrahydrofuran, dimethylformamide, dimethyl sulphoxide and dichloromethane. The molecular weights of the polymers were in the range of 9000–12,000 g mol⁻¹. The trans-cis photoisomerization of the polymer were studied both under UV radiation and dark. The isomerization rate constants were found to be in the range of 0.7–1.4 \times 10⁻² sec⁻¹ and 7.0 \times –2.5 \times 10⁻⁵ sec⁻¹.

INTRODUCTION A very active research field is represented by the studies on azobenzene containing liquid crystalline polymers.¹⁻⁴ The reversible trans-cis photoisomerization of the azo-benzene can be utilized to design new advanced materials coupled with understanding of new phenomenon and its underlying mechanisms. The resulting materials have wide range of applications such as optical data storage and other device applications.^{1–7} A recent discovery by Ikeda and coworkers illustrates the light directed bending and unbending of thin films of crosslinked azobenzene liquid crystalline polymer which can be used as an actuator for microdevice applications.⁸ Surface relief grating (SRG) is an example reported by two groups independently in 1995.9,10 Recently, azo polymers are being synthesized with diverse architectures such as dendrimers,¹¹ proteins,¹² micelles,¹³ and solgel materials¹⁴ for studying the photoactivity directed applications.

In our earlier work linear siloxane polymers having azo side group have been synthesized and characterized.¹⁵ The polymers were observed to undergo tran-cis isomerization at a very high rate. The polymers were further analyzed for their photomechanical properties. The rate was found to be quite encouraging. Encouraged by the result, further study was planned by synthesizing hyperbranched polymers containing both siloxane and azo moieties. A good number of reports are available in literature on hyperbranched polymer in general The thermotropic behavior of the polymers was studied by using polarizing optical microscopy and differential scanning calorimetry, respectively. The polymers P1 and P2 showed liquid crystalline texture characteristic of nematic phase. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 2659–2668, 2012

KEYWORDS: azo polymers; click chemistry; hyperbranched; liquid crystalline; liquid-crystalline polymers (LCP); nematic; photo-chemistry; photoswitching; polysiloxanes; UV-vis spectroscopy

and photoactive polymer in particular. Synthesis and characterization of branched LC polymers containing disc like mesogens¹⁶ and rod-like mesogens based on conformational isomerism^{17,18} were reported for the first time by Percec et al. The electrophilic cyclotetramerization polymerization of 3,4-bis(*n*-alkyloxy) benzyl alcohol with an α,ω -bis{[2-(alkoxy)-5-(hydroxymethyl)phenyl]oxy} alkane¹⁶ resulted in hyperbranched polymer with cyclotetraveratrylene units in the branching points. Synthesis of hyperbranched 10-bromo-1-(4-hydroxy-4'-biphenylyl)-2-(4-hydroxyphenyl) decane (TPDb) based polymers demonstrating the dependence of phase behavior on the nature of their chain end was also reported.¹⁷ Synthesis of dendrons up to fourth generation and their phase behavior study were also reported.¹⁹ Viscoelastic properties of dilute nematic mixtures containing cyclic and hyperbranched liquid crystalline polymers dissolved in a nematic solvent were studied.²⁰ Rational design for the first nonspherical dendrimers showing calamitic nematic and smectic phases was reported by Percec et al.²¹ The dramatic stabilization of hexagonal columnar mesophase was generated from supramolecular and macromolecular columns, respectively.²² Design of first spherical supramolecular dendrimers which self organize into cubic LC phase²³ and controlling polymer shape through self assembly of dendritic side group²⁴ appeared in quick succession. The individual spherical and cylindrical supramolecular dendrimers started getting confirmed

© 2012 Wiley Periodicals, Inc.



directly by using X-ray diffraction analysis.²⁵ Synthesis and structural analysis of two constitutional isomeric libraries of AB₂ based monodendrons and supramolecular dendrimers were also reported.²⁶ Regardless of repeat unit on their periphery, the first three or four generations of monodendrons self assembled in to supramolecular dendrimers. Self-organization of supramolecular helical dendrimers in to complex electronic material and amphiphilic dendritic dipeptides in to helical pores were reported by Percec et al.^{27,28} Later, selfassembled nanostructures obtained from natural and synthetic amphiphiles were shown to mimic biological membranes having stability and mechanical strength.²⁹ Design principles of self assembled dendrons via the primary structures generated form combinations of (AB)_v-AB₃ and (AB)_v-AB₂ building blocks were reported to produce largest structural and dimensional diversity of supramolecular dendrimers.³⁰ Synthesis and retrostructural analysis of libraries of AB₃ and constitutional isomeric AB₂ phenylpropyl ether based supramolecular dendrimer was also reported thereafter.³¹ The dependence of shape of heat shrinking spherical and columnar supramolecular dendrimers and their interconversion on molecular taper angle is also reported.³² Self-assembly of semifluorinated tapered monodendrons containing crown ethers into supramolecular columnar dendrimers exhibiting a homeotropic hexagonal columnar liquid crystalline phase was also reported to be induced by fluorophobic effect.33 Review on dendron-mediated self-assembly, disassembly, and self-organization of complex systems is also reported by Percec and coworkers.³⁴ Most of the reported method of polysiloxane synthesis only demonstrates hydrosilylation as the most used polymerization method. Considering the advantages of click chemistry such as low susceptibility to side reactions, mild reaction conditions, nearly quantitative yields, broad tolerance toward functional groups it has become one of the most preferred route for synthesis of polymers. The synthesis of a number of polymeric materials such as dendrimers, block copolymers, complex macromolecular structures via click chemistry have been reported.35-38 The reports on synthesis of hyperbranched polymers through click chemistry are still scarce and most of them were synthesized by A₂B₃ approach³⁹ where two monomers containing diazido and divne groups were used for the synthesis. The Cu(I)-catalyzed click polymerizations of the AB₂ monomers were found to yield insoluble polymers due to self-oligomerization.⁴⁰ Azo moieties in the form of A2B type monomer self polymerized to hyperbranch architecture,^{41,42} Click chemistry have also been utilized for the synthesis of other hyperbranched polymers using A₂B approach.^{43,44} Similarly azo moieties can be used as an A₂ monomer which will polymerize with B₃ monomer to get A₂B₃ hyperbranched polymer through click chemistry route. In this report effort has been made to utilize click chemistry to make hyperbranched siloxane azo polymers and characterize them. To the best of our knowledge, for the first time we have made azo triazide as a B₃ moiety and polymerized it with poly dimethyl siloxane-diyne (PDMS-diyne) which is A2 moiety to get soluble liquid crystalline photoactive

hyperbranched polymers which fulfils the characteristics required for both liquid crystallinity and photoactivity coupled with good solubility in solvents.

EXPERIMENTAL

Materials

Propargyl bromide, hydride terminated polydimethyl siloxane $(M_n = 580)$, 2% platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex in xylene (karstedt's catalyst), *n*,*n*-bis(die-thanol)aniline, sodium-ascorbate, 4,4-dimethyl amino pyridine (DMAP), dicyclohexyl carbodimide (DCC), allyl alcohol, 4-chloro-butan-1-ol, 6-chloro-hexan-1-ol, 8-chloro-octan-1-ol were purchased from Sigma-Aldrich. *p*-Amino benzoic acid, phosphorus oxychloride (POCl₃) and all other chemicals were purchased from S D fine chemicals, India. All solvents were purchased from Merck India. THF and toluenes were dried over sodium-ketyl radical. All chemicals were used as received without further purifications unless otherwise specified.

Characterization

UV-visible spectra of the polymers were taken on a Cary 500 Scan UV-vis-NIR spectrophotometer. ¹H and ¹³C NMR spectra of the monomers and ¹H NMR of polymers were recorded on either a 400 or 500 MHz Bruker-FT NMR spectrometer. Heating / cooling rate used for all DSC analysis was 10 °C/min. For studying the liquid crystalline behavior, a Leica DMLD, optical polarizing microscope with image analyzer equipped with LINKAM TMS 94 hot stage and LINKAM LNP controlling unit was used. For photoresponsive and photomechanical studies, the samples were irradiated in the cabinet of a UV chamber (Spectrolinker XL – 1500) fitted with 6×15 Watt medium pressure mercury bulbs. The sample was placed at a distance of 15 cm from source and irradiated for various time intervals. For preparation of sample for photomechanical study the silicone polymers were blended with poly methyl methacrylate (PMMA) in solution phase and cast as a film on a rubbed glass plate

METHODS

The synthesis of PDMS-diyne and azo-triazide is shown in scheme I. The synthesis of methyl 4-(prop-2-ynyloxy) benzoate (**1**), 4-(prop-2-ynyloxy) benzoic acid. (**2**), *N*,*N*-bis(2-chloroethyl)-aniline (**5**), 4-((4-bis(2-chloroethyl) amino) phenyl) diazenyl) benzoic acid (**6**), was carried out by following the procedure as reported earlier.^{15,45}

PDMS-diol (3)

Allyl alcohol (11.0 g, 190 mmol) was mixed with anhydrous toluene (25 mL) under inert condition in 100 mL R.B. flask and maintained at 50 °C. Karstedt's catalyst (0.44 mL) was added to the mixture through rubber septum using a syringe. Hydride terminated PDMS (27.5 g, 47.4 mmol) was added dropwise through syringe via rubber septum to the reaction mixture. The temperature was raised further to 80 °C and continued until disappearance of Si—H peak at 2163 cm⁻¹ in FTIR spectra. Excess of toluene and allyl alcohol was removed by distillation under reduced pressure. The residue was diluted with dichloromethane and passed over alumina to remove the platinum catalyst. The filtrate was concentrated by evaporating solvent in rotavapor.

ARTICLE



i) Propargyl bromide, K₂CO₃, DMF; ii) aq. N aOH, THF, M eOH; iii) Allyl alcohol, karstedt's catalyst; iv) Compound 2, DCC, DMAP, anh. THF; v) POCI₃ re flux; vi) N aNO₂, HCI, 0-5 °C; vii) DCC/DMAP, CI-(CH₂)_n-OH, anh. THF,R.T; viii) NaN₃, DMSO, 90°C

SCHEME 1 Synthesis of PDMS-diyne and azo-triazide monomers.

Yield: 32 g, (97 %) ¹H NMR (400 MHz, $CDCl_3$) δ : 0.02 (bs, 56H), 0.51 (t, J = 8.6 Hz, 4H), 1.55 (p, 7.5 Hz, 4H), 2.37 (bs, 2H), 3.54 (t, J = 6.7 Hz, 4H); ¹³C NMR (125 MHz, $CDCl_3$): 0.9, 1.8, 13.8, 26.3, 65.2.

PDMS-diyne (4)

A THF solution (25 mL) of 4-(prop-2-ynyloxy) benzoic acid (2) (10.11 g, 57.47 mmol), PDMS-diol (3) (10 g, 14.37 mmol), and DMAP (0.26 g, 2.15 mmol) was taken in a 100 mL two necked R.B.flask and nitrogen passed continuously. A solution of DCC (4.45 g, 21.55 mmol) in 5 mL of THF was added to the reaction mixture through septum using syringe. The mixture was allowed to stir at room temperature. It was filtered and the filtrate was evaporated. The crude compound was purified by column chromatography by using a mixture of petroleum ether and ethyl acetate (98 : 2, v/v) as eluant to obtain the product as colorless oil.

Yield: 12 g, (82.4%); ¹H NMR (500 MHz, CDCl₃) δ : 0.03 (s, 6H), 0.09 (s, 12H), 0.61 (t, J = 8.5 Hz, 4H), 1.76 (q, J = 7.0

Hz, 4H), 2.53 (t, J = 2.0 Hz, 2H), 4.23 (t, J = 6.5 Hz, 4H), 4.72 (d, J = 4.0 Hz, 4H), 6.98 (d, J = 9.0 Hz, 4H), 8.0 (d, J = 9.0 Hz, 4H); ¹³C NMR (125 MHz, CDCl₃) δ : 1.14, 1.24, 14.13, 22.74, 55.77, 67.13, 76.00, 77.83, 114.41, 123.81, 131.45, 161.04, 166.14.

Chlorobutyl 4-((4-bis(2-chloroethyl) amino) phenyl) diazenyl) benzoate (7)

4-((4-bis(2-chloroethyl) amino) phenyl) diazenyl) benzoic acid (2 g, 5.46 mmol), 4-chloro-1-butanol (3) (0.71 g, 6.58 mmol), DMAP (0.1 g, 0.81 mmol) and 25 mL of anhydrous THF were taken in a 100 mL R.B.flask. A solution of DCC (1.6 g, 8.2 mmol in 5mL of THF) was added to the reaction flask through septum via syringe. The mixture was allowed to stir under nitrogen for 24 h. It was filtered and the filtrate was evaporated. The crude material was purified by column chromatography using a mixture of petroleum ether and ethyl acetate (95 : 5 v/v) as eluant to obtain the product as red colored solid.





SCHEME 2 Synthesis of azo containing siloxane hyperbranched polymers by click chemistry.

Yield: 2.28g (84%); ¹H NMR (500 MHz, CDCl₃) δ : 8.14 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 9.0 Hz, 2H), 4.38 (t, J = 6.5 Hz, 2H), 3.70 (t, J = 6 Hz, 4H), 3.57 (t, J = 6Hz, 4H), 3.38 (t, J = 6.5 Hz,2H), 1.89 (p, J = 6.5 Hz, 2H), 1.78 (p, J = 7.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ : 25.64, 26.03, 48.77, 50.75, 51.02, 64.34, 111.87, 122.14, 125.69, 130.49, 130.60, 144.61, 149.30, 155.74, 166.13.

Chlorohexyl 4-((4-bis(2-chloroethyl) amino) phenyl) diazenyl) benzoate (8)

The synthesis was carried out by similar procedure as mentioned for compound 7. In this case 4-chloro-1-butanol was replaced by 6-chloro-1-hexanol.

Yield: 2.50g (91%); ¹H NMR (500 MHz, CDCl₃) δ : 8.14 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H),



FIGURE 1 ¹H NMR spectra of PDMS-diyne.

ARTICLE



FIGURE 2 ¹H NMR spectra of polymer P2.

6.80 (d, J = 9.5 Hz, 2H), 4.34 (t, J = 6.5 Hz, 2H), 3.69 (t, J = 6 Hz, 4H), 3.57 (t, J = 6.5 Hz, 4H), 3.28 (t, J = 7.0 Hz, 2H), 1.81 (p, J = 6.5 Hz, 2H), 1.64 (p, 7.0 Hz, 2H), 1.45–1.51 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ :25.64, 26.40, 28.59, 28.74, 48.80, 50.76, 51.33, 111.87, 122.11, 125.67, 130.47, 130.85, 144.62, 149.27, 155.69, 166.23.

Chlorooctyl 4-((4-bis(2-chloroethyl) amino) phenyl) diazenyl) benzoate (9)

The synthesis was carried out by similar procedure as mentioned for compound 7. In this case 4-chloro-1-butanol was replaced by 8-chloro-1-octanol.

Yield: 2.55g (88 %); ¹H NMR (500 MHz, CDCl₃) δ : 8.14 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 9.0 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 4.33 (t, J = 6.5 Hz, 2H), 3.69 (t, J = 6 Hz, 4H), 3.56 (t, J = 6.0 Hz, 4H), 3.25 (t J =, 7.0 Hz, 2H), 2.61 (s, 2H), 1.78 (p, J = 7.0 Hz, 2H), 1.60 (p, J = 7.0 Hz, 2H), 1.33–1.41 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ : 25.91, 26.60, 28.65, 28.77, 28.99, 29.09, 40.95, 48.77, 50.75, 51.41, 65.15, 111.86, 122.09, 125.66, 130.46, 130.93, 144.60, 149.27, 155.65, 166.25.



FIGURE 3 DSC thermogram of polymers P1 and P2.

Azidobutyl 4-((4-bis(2-azidoethyl) amino) phenyl) diazenyl) benzoate (10)

To a solution of (6) (0.9 g, 2.0 mmol) in DMSO (10 mL) sodium azide (0.65 g, 10.0 mmol) was added. The reaction mixture was heated at 90 °C for 10 h and cooled to R.T. and poured in to dilute HCl (5%, 15 mL). The compound was extracted with dichloromethane. The organic layer was washed with water, dried over Na_2SO_4 and evaporated under vacuum. Purification of the product was done by column chromatography using petroleum ether and ethyl acetate mixture (95 : 5; v/v).

Yield: 0.91 g (97%); ¹H NMR (500 MHz, CDCl₃) δ : 8.14 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 4.39 (t, J = 5.0 Hz, 2H), 3.85 (t, J = 7 Hz, 4H), 3.70 (t, 7 J =.0 Hz, 4H), 3.63 (t, J = 5.0 Hz, 2H), 2.61 (s, 2H), 1.97 (p, J = 2.5 Hz, 2H), 1.60 (p, J = 7.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ :26.16, 29.24, 40.17, 44.76, 53.45, 64.24, 111.62, 122.16, 125.72, 130.50, 130.68, 144.68, 149.10, 155.70, 166.13.

Azidohexyl 4-((4-bis(2-azidoethyl) amino) phenyl) diazenyl) benzoate (11)

The synthesis was carried out by using same procedure as mentioned for product 10. In this case 4-chloro-1-butanol was replaced by 6-chloro-1-hexanol.

Yield: 0.96 g (97 %); ¹H NMR (500 MHz, CDCl₃) δ : 8.15 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 4.35 (t, J = 6.5 Hz, 2H), 3.85 (t, J = 7.5 Hz,

TABLE 1 Physico-Chemical Properties of Polymers

Polymer	Thermal Transition (DSC)ª	POM ^b T _i	<i>M</i> _n	M _w	M _w /M _n
P1	4 N 63 I	70	11,300	20,400	1.80
P2	2 N 66 I	69	9,900	14,400	1.47
P3	-	-	9,800	14,900	1.49

 a Transition temperature identified from heating cycle with DSC (at a heating rate of 10 $^\circ\text{C/min}$ under N_2 atm).

^b Transition temperature identified with POM at a heating rate of 5 °C/min. ${}^{c}T_{i}$ = isotropization temperature.



FIGURE 4 POM images showing nematic droplets texture for P1 at temperature 30 °C (A) and 45 °C (B).

4H), 3.70 (t, J = 7.0 Hz, 4H), 3.55 (t, J = 5.0 Hz, 2H), 1.79–1.84 (m, 4H), 1.49–1.56 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ : 25.39, 26.54, 28.57, 32.43, 40.17, 44.90, 53.44, 111.62, 122.13, 125.70, 130.48, 130.91, 144.68, 149.07, 155.63, 166.22.

Azidooctyl 4-((4-bis(2-azidoethyl) amino) phenyl) diazenyl) benzoate (12)

The synthesis was carried out by using same procedure as mentioned for product 10. In this case 4-chloro-1-butanol was replaced by 8-chloro-1-octanol.

Yield: 1.00g (96%); ¹H NMR (500 MHz, CDCl₃) δ : 8.15 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 9.5 Hz, 2H), 4.34 (t, J = 7.0 Hz, 2H), 3.85 (t, J = 7.0 Hz, 4H), 3.70 (t, J = 7.0 Hz, 4H), 3.53 (t, J = 6.5 Hz, 2H), 1.75–1.82 (m, 4H), 1.33–1.49 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ : 25.91, 26.75, 28.66, 28.73, 29.07, 32.55, 40.18, 45.07, 53.44, 65.17, 111.62, 122.12, 125.70, 130.47, 131.00, 144.68, 149.07, 155.61, 166.24.

Synthesis of Polymers by Click-Polymerization (P1)

Scheme 2 shows the synthesis of azo-siloxane polymer by click chemistry route.

A mixture of PDMS-diyne (4) (0.1 g, 0.09×10^{-2} mmol), azidobutyl 4-((4-bis(2-azidoethyl) amino) phenyl) diazenyl) ben-



FIGURE 5 UV–visible absorption spectra in chloroform solution for trans-cis isomerization of Polymer P2.

zoate (10) (0.052 g, 0.09×10^{-2} mmol) and sodium ascorbate (0.041 g, 0.20 mmol) was taken in 3 mL THF. The mixture was allowed to stir under nitrogen atmosphere for 10 min. A solution of copper sulfate (0.027 g, 0.108 mmol) in 3 mL water was added to it. The reaction mixture was stirred for additional 40 mins under N₂ atmosphere and quenched with methanol (20 mL). The ppt was filtered, dissolved in THF and passed through alumina bed to remove the catalyst and insoluble impurities. The THF solution was then evaporated to obtain the polymer (P1) as red powder. Similarly polymers P2 and P3 were synthesized by reacting (4) with (11) and (12), respectively.

P1

Yield: 0.12 g, (81.0%); ¹H NMR (500 MHz, CDCl₃) δ : 0.00 - 0.07 (bs), 0.61 (bs, 4H), 0.88 (bs, 8H), 1.25–2.26 (br, 6H), 3.38 (bs, 4H), 3.59–3.64 (bs, 6H), 4.23 (bs, 2H), 4.39 (bs, 4H), 5.22 (bs, 4H), 6.68–6.97 (br, 10H); 7.45 (bs, 1H), 7.90–8.15 (br, 6H).

P2

Yield: 0.11g, (79.3%); ¹H NMR (500 MHz, CDCl₃) δ : 0.00 - 0.07 (bs), 0.61 (bs, 4H), 0.89–1.25 (bs, 8H), 1.26–1.77 (br, 10H), 3.28 (bs, 4H), 3.60–3.64 (bs, 6H), 4.23 (bs, 2H), 4.35–4.40 (bs,



FIGURE 6 UV-visible absorption spectra in chloroform solution for cis-trans isomerization of Polymer P2.

(br, 6H).



FIGURE 7 Plot of InA versus time for trans-cis isomerization of Polymers.

4H), 5.23 (bs, 4H), 6.68–6.97 (br, 10H); 7.45 (bs, 1H), 7.90–8.15 (br, 6H).

P3

Yield: 0.12g, (78.6%); ¹H NMR (500 MHz, CDCl₃) δ : 0.00 - 0.07 (bs), 0.60 (bs, 4H), 0.89–1.25 (bs, 8H), 1.37–2.26 (br, 14H), 3.26 (bs, 4H), 3.59 (bs, 6H), 4.22 (bs, 2H), 4.34 (bs, 4H)

RESULTS AND DISCUSSION

Synthesis and Characterizations

Hyperbranched siloxane polymers having azo moieties were synthesized via click chemistry technique and thoroughly characterized for chemical structure, liquid crystallinity, and photoresponsive behavior. The design of the hyperbranched polymer was done by reacting azo-triazide and siloxanediyne (PDMS-diyne). This study was done to find out the variation in properties as a function of change of architecture from linear to hyperbranched one. The synthesis of azo-triazide is also targetted in the study which is not reported so far. Keeping in view the polymer property requirement for photoactuation, siloxane is used as a part of backbone for maintaining flexibility of the polymer during photoactuation process. Azo moieties acts as mesogens due to its rigid rod like nature which is aided by flexible siloxane spacer to enable liquid crystalline phase generation. Further, the azo molecule undergoes trans-cis isomerization on irradiation. The mesogenic behavior and photoactivity coupled together enable the polymer to exhibit photoactuation on irradiation.

5.25 (bs, 4H), 6.68-6.97 (br, 10H); 7.45 (bs, 1H), 7.87-8.15

For the synthesis of polymers, reactions were carried out between PDMS-divne and three different types of azo-triazido to give three polymers P1-P3. To attach third azide group to azo benzene carboxylic acid (6), -COOH group was esterified with aliphatic chloroalcohol. The alkyl chain of chloroalcohol was varied to make P1, P2, and P3. The LC properties and photoswitching behavior of the polymers are studied in this work. The synthesis of PDMS-diyne, was done through four step synthetic procedure as shown in Scheme 1 similar to synthesis of trisiloxane-diol reported by us in our earlier work.15 It was synthesized through esterification between PDMS-diol (3) and 4-(prop-2-ynyloxy) benzoic acid (2) using DCC/DMAP catalyst. Figure 1 shows ¹H NMR spectra of PDMS-diyne. The disappearance of hydroxyl peak centered at $\delta = 2.37$ is observed in esterified compound. The esterification is also confirmed by the shifting of Si-CH₂, Si-CH2-CH2, and Si-CH2-CH2-CH2 peaks downfield in the spectra.

For the synthesis of B_3 (azo-triazide), the intermediate 4-((4bis(2-chloroethyl) amino) phenyl) diazenyl) benzoic acid (6) was synthesized as described by Shen et al.⁴⁵ The obtained acid (6) was esterified separately with three different alcohols (4-chloro-1-butanol, 6-chloro-1-hexanol, 8-chloro-1-octanol) to get three different trichloro-azo compound (7, 8, 9) using DCC/DMAP catalyst in dry THF solvent. The product was thoroughly characterized by ¹H NMR and ¹³C NMR spectroscopy. Further, the trichloro-azo moieties were converted to azo-triazide moieties (B_3) using sodium azide in DMSO. The product was thoroughly characterized from the characteristic peaks in ¹H NMR and ¹³C NMR spectra. The conversion of tri-chloro azo to azo triazide (**10-12**) is confirmed by downfield shifting of the peak positions in ¹H NMR and ¹³C NMR spectra respectively.



Polymers	$λ_{max}$ (nm) ^a π-π*	$\lambda_{max} (nm)^a n - \pi^*$	$K_{\rm x}~({\rm s}^{-1})^{\rm b}$	$K_{ m y}~(m sec^{-1})^{ m c}$	K_{z} (min ⁻¹) ^d
P1	405	526	0.7×10^{-2}	$1.8 imes 10^{-3}$	$7.0 imes 10^{-5}$
P2	406	525	1.1×10^{-2}	$2.8 imes 10^{-3}$	$5.0 imes10^{-5}$
P3	406	525	1.4×10^{-2}	$5.8 imes10^{-3}$	$2.5 imes 10^{-5}$

TABLE 2 The Rate Constants of the Polymers for Trans – Cis and Cis – Trans Isomerization

^a Recorded in chloroform solution.

^b Rate constant calculated from the first slope of trans to cis isomerization graph (InA vs. Time).

^c Rate constant calculated from the second slope of trans to cis isomerization graph (InA vs. Time).

^d Rate constant calculated from the slope of cis to trans isomerization for initial 30 min of dark relaxation.(InA vs. Time).

The polymerization was carried out by taking equimolar amount of PDMS-diyne (4) and the azo-triazide (10-12), along with copper-sulphate and sodium ascorbate in THF/ H_2O (2 : 1; v/v). The polymerization reaction was completed in less than 1 hour time and highly viscous polymer solution resulted. The ¹H NMR spectra shows the appearance of a peak around 7.45–7.50 ppm which is attributed to the proton in triazole ring (Fig. 2).

From the GPC results, the molecular weights (M_n) of the polymers are found to be in the range of 9000–12,000 g mol⁻¹. The overall yield of the soluble polymer increases from P1 to P3 to a maximum of 80–85%. All the polymers are soluble in organic solvents like THF, DMF, DCM, and DMSO.

DSC Study

Figure 3 shows the DSC thermogram of polymers P1-P2 and the data are incorporated in Table 1. Both the polymers exhibit two thermal transitions. The first thermal transition can be attributed to glass transition temperature. The polymer P1 exhibited slightly higher glass transition temperature of 4 °C compared to polymer P2 showing at 2 °C. However, the difference is very small. This could be attributed to almost similar flexibility of the alkane chain (C4 and C6) attached to the esters of the azo moiety in polymer P1 and P2. In polymer P3 the glass transition temperature is found to be at -2 °C which has alkyl chain (C8) which is reasonably flexible. The second endotherm in the DSC thermogram



FIGURE 8 Three-dimensional structure of monodendron of Polymer P2.

of P1 and P2 can be attributed to isotropization. The isotropization temperatures of P1 and P2 lie at 63 °C and 66 °C, respectively. This may be due to slightly higher orientation originated from higher alkane tail in polymer P2 enabling LC phase to exist up to higher temperature compared to polymer P1. The polymer P3 does not show any LC transition. This may be due to too much flexibility of the polymer which is not conducive for LC ordering.

POM Study

The mesogenic behavior was studied by POM. Thin layer of the polymer was prepared on a glass slide by slow evaporation of their chloroform solution and further drying the film under vacuum. The thin film was kept on hot stage of the POM and changes in texture with heating were observed. The representative POM micrographs are shown in Figure 4 and the observation is summarized in Table 1. For polymer P1 appearance of texture, characteristic of nematic phase, is observed. For polymer P2 similar nematic texture appears. The isotropization temperatures of P1 and P2 are observed to be at 70 °C and 69 °C, respectively. This is similar to that observed in DSC study.

Photo Responsive Properties

Before carrying out photoirradiation study, the polymer solution was kept in dark for 3 days to assume 100% trans form of the azobenzene. The λ_{max} absorbance maxima was recorded around 406 nm for the polymers. The absorbance at 406 nm is due to π - π^* transition of stable trans form. The isomerization behavior was studied by irradiating the polymer solutions with UV light (365 nm) for different time intervals and the absorbance versus wavelength was plotted. As described in our earlier report two absorbance peaks are observed in UV-visible spectra for all the polymers (Fig. 5) during irradiation. The peaks at around 400 nm and 500 nm, respectively are attributed as to π - π^* and n- π^* transitions respectively. Further the n- π^* transition is found to be more intense as compared to the usually observed intensity.

TABLE 3 Energy Calculation of the Polymers from the

 Molecular Modeling and Simulations Studies

Polymers	Total Energy (Kcal/mol)
P1	565.25
P2	557.24
P3	693.65



FIGURE 9 Photomechanical bending of polymer P1 under irradiation with UV light (a) before irradiation (b) after irradiation.

During irradiation, the absorbance due to π - π * electronic transition decreases and $n-\pi^*$ transition increases indicating conversion of trans to cis form of the azo polymer. Figure 6 shows the change of absorbance with time for cis-trans isomerisation in dark. The rate constants of isomerization of the polymers are calculated from slope of the plot of ln A versus time (Fig. 7). The polymers are found to isomerize within short time to cis form. Shouldering is observed in cis peak at higher wave length during conversion of trans to cis form. This can be attributed to solvatochromism.^{15,46} the polar interaction of cis azo shifts the absorption spectra to higher wave length.⁴⁶ The isomerization process is also studied for cis to trans interconversion for all the three polymers. For this process, the chloroform solution of polymers was kept under UV irradiation until complete disappearance of π - π * electronic transition is observed in UV-vis spectra. The solution was kept in dark and periodic recording of UV-vis spectra was done. lnA is plotted versus time for the polymers. Two slopes (K_x, K_y) $K_{\rm v}$) are observed for trans-cis isomerization (Fig. 7). The rate constants for trans-cis isomerization increases with increase in chain length attached to the ester group of azo moiety for P1-P3. It may be due to ease in isomerization with increase in the flexibility. As the alkyl chain length attached to the azo group increases the flexibility which, in turn, enhances the isomerization. Only one slope is observed for cis to trans isomerization. This may be due to very slow nature of the conversion. Table 2 summarizes the values of rate constants for trans to cis isomerization and back.

Molecular Modeling Study of Model Compound

Due to the striking similarities of oligomers with polymers, the monodendrons of the polymers have been constructed using molecule-building tools in the Accelrys Materials Studio. The optimization of geometry and calculation of energies were performed by using Material Studio 4.4 version (Accelrys software). All the polymers structures were constructed in material studio and atom based, polymer consistent force field (PCFF) forcite calculation was adopted to carry out the simulation. The Figure 8 shows the threedimensional structure of monodendron of polymer.

The calculated energy of synthetic polymers depends strongly on the conformational statistics of the polymer chains. The total energy is contributed by

$$V = \sum_{\text{valence energy}} V_{\text{diag.terms}} + \sum_{\text{valence energy}} V_{\text{cross terms}} + \sum_{\text{nonbonded energy}} V_{\text{nonbonded energy}}$$

The total energies found from this study are summarized in Table 3. It can be observed that the total energy of polymer



Photomechanical Bending

All the polymer P-P3 are found to be having glass transition temperature around -4 to +6 °C therefore mechanical strength of the free standing film was very poor and unsuitable for photomechanical study. To check its photomechanical properties it was blended with PMMA and the blend film was irradiated with UV light. Silicone Azo-PMMA blend film on irradiation by 365 nm UV light has shown appreciable bending. The photoactuation of the polymers were studied by irradiation with 365 nm irradiation and typical irradiation intensity of 5500–6500 μ W/cm². As can be observed from the Figure 9 the flat film gets bend after 20 mins of irradiation.

CONCLUSIONS

Three types of hyperbranched siloxane polymers possessing photoactive azo moiety, were synthesized using click chemistry route. The polymers have showed liquid crystalline characteristic of nematic phase. All the three polymers showed photoisomerization properties. The trans-cis conversion is very fast. During the process one shoulder peak, at wavelength higher than the cis peak, was observed due to solvatochromism. The rate constants for trans to cis isomerization increases with increase in the aliphatic chain length attached to ester of azo moieties. The rate constant for cis-trans conversion is very slow. The rate constant pattern is exactly reversed as compared to trans-cis conversion. This was confirmed by the energy calculation for the polymers; P3 showing highest energy. Photomechanical bending was also observed in polymer P1 on blending it with PMMA after irradiation with UV light.

REFERENCES AND NOTES

1 Ichimura, K. Chem. Rev. 2000, 100, 1847-1873.

2 Viswanathan, N.; Kim, D. Y.; Bian, S.; Williams, J.; Liu, W.; Li, L.; Samuelson, L.; Kumar, J.; Tripathy, S. K. *J. Mater. Chem.* **1999**, *9*, 1941–1955.

3 Natansohn, A.; Rochon, P. Chem. Rev. 2002, 102, 4139-4176.

4 Ikeda, T. J. Mater. Chem. 2003, 13, 2037-2057.

5 Eich, M.; Wendorff, J. H. *Makromol. Chem. Rapid. Commun.* 1987, *59*, 467–471.

6 Fischer, T. L.; Lasker, M.; Rutloh, C. S.; Stumpe, J. *Mol. Cryst. Liq. Cryst.* 1997, *299*, 293–299.

7 Hvilsted, S.; Andruzzi, F. C.; Fulinna, H.; Siesler, W.; Ramanujam, P. S. *Macromolecules* **1995**, *28*, 2172–2183.

8 Yu, Y.; Nakano, M.; Ikeda, T. Nature 2003, 425, 145-156.

9 Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136–138.

10 Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar. J. *Appl. Phys. Lett.* **1995**, *66*, 1166–1168.

11 Junge, D. M.; McGrath, D. V. *J. Am. Chem. Soc.* **1999**, *121*, 4912–4913.



12 Liang, X.; Asanuma, H.; Komiyama, M. J. *Am. Chem. Soc.* **2002**, *124*, 1877–1883.

13 Orihara, Y.; Matsumura, A.; Saito, Y.; Ogawa, N.; Saji, T.; Yamaguchi, A.; Sakai, H.; Abe, M. *Langmuir* **2001**, *17*, 6072–6076.

14 Chaumel, F. H.; Jiang, K. A. *Chem. Mater.* 2001, *13*, 3389–3395.

15 Pandey, S.; Kolli, B.; Mishra, S. P.; Samui, A. B. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 1205–1215.

16 Percec, V.; Cho, C. G.; Pugh, C.; Tomazos, D. *Macromolecules* 1992, *25*, 1164–1176.

17 Percec, V.; Kawasumi, M. *Macromolecules* **1992**, *25*, 3843–3850.

18 Percec, V.; Chu, P.; Kawasumi, M. *Macromolecules* **1994**, *27*, 4441–4453.

19 Percec, V. Pure Appl. Chem. 1995, 67, 2031-2038.

20 Chen, F.-L.; Jamieson, A. M.; Kawasumi, M.; Percec. V. J. Polym. Sci. Part B: Polym. Phys. 1995, 33, 1212–1223.

21 Percec, V.; Chu, P.; Ungar, G.; Zhod, J. J. *Am. Chem. Soc.* **1995**, *117*, 11441–11454.

22 Percec, V.; Schlueter, D.; Kwon, Y. K.; Blackwell, J. *Macro-molecules* 1995, *28*, 8807–8818.

23 Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. J. *Am. Chem. Soc.* 1997, *119*, 1539–1555.

24 Percec, V.; Ahn, C. H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* 1998, *391*, 161–164.

25 Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. S. K. *Science* **1997**, *278*, 449–452.

26 Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. J. Am. Chem. Soc. 2001, 123, 1302–1315.

27 Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyanovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H.-W.; Hudson, S. D.; Duan, H. *Nature* **2002**, *417*, 384–387.

28 Percec, V.; Dulcey, A. E.; Balagurusamy, V. S. K.; Miura, Y.; Smidrka, J.; Peterca, M.; Nummelin, S.; Edlund, U.; Hudson, S. D.; Heiney, P. A.; Duan, H.; Magonov, S. N.; Vinogradov, S. A. *Nature* **2004**, *430*, 764–768.

29 Percec, V.; Wilson, D. A.; Leowanawat, P.; Wilson, C. J. Hughes;, A. D. Kaucher, M. S.; Hammer, D. A.; Levine, D. H.; Kim, A. J.; Bates, F. S.; Davis, K. P.; Lodge, T. P.; Klein, M. L.; DeVane, R. H.; Aqad, E.; Rosen, B. M.; Argintaru, A. O.; Sienkowska, M. J.; Rissanen, K.; Nummelin, S.; Ropponen, J. *Science* 2010, *328*, 1009–1014.

30 Percec, V.; Mitchell, C. M.; Cho, W.-D.; Uchida, S.; Glodde, M.; Ungar, G.; Zeng, X.; Liu, Y.; Balagurusamy, V. S. K.; Heiney, P. A. *J. Am. Chem. Soc.* **2004**, *126*, 6078–6094.

31 Percec, V.; Peterca, M.; Sienkowska, M. J.; Ilies, M. A.; Aqad, E.; Smidrkal, J.; Heiney, P. A. *J. Am. Chem. Soc.* **2006**, *128*, 3324–3334.

32 Ungar, G.; Percec, V.; Holerca, M. N.; Johansson, G.; Heck, J. A. *Chem. Eur. J.* **2000**, *6*, 1258–1266.

33 Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. J. *Am. Chem. Soc.* **1996**, *118*, 9855–9866.

34 Rosen, B. M., Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. *Chem. Rev.* **2009**, *109*, 6275–6540.

35 (a) Gao, H.; Louche, G.; Sumerlin, B. S.; Jahed, N.; Golas, P.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 8979–8982; (b) Sumerlin, B. S.; Tsarevsky, N. V.; Louche, G.; Lee, R. Y.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 7540–7545; (c) Lutz, J. F.; Börner, H. G.; Weichenhan, K. *Macromol. Rapid Commun.* **2005**, *26*, 514–518.

36 (a) Binder, W. H.; Kluger, C. *Macromolecules* **2004**, *37*, 9321–9330; (b) Bock, V. D.; Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2006**, 51–68; (c) Sawa, M.; Hsu, T.-L.; Itoh, T.; Sugiyama, M.; Hanson, S. R.; Vogt, P. K.; Wong, C.-H. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 12371–12376; (d) Altintas, O.; Hizal, G.; Tunca, U. J. *Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 5699–5706.

37 (a) O'Reilly, R. K.; Joralemon, M. J.; Hawker, C. J.; Wooley, K.L. *New J. Chem.* **2007**, *31*, 718–724; (b) Malkoch, M.; Schleicher, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P.; Wu, P.; Fokin, V.V. *Macromolecules* **2005**, *38*, 3663–3678; (c) Binder, W. G.; Sachsenhofer, R. *Macromol. Rapid Commun.* **2008**, *29*, 952–981; (d) Bu, H.-B.; Götz, G.; Reinold, E.; Vogt, A.; Schmid, S.; Blanco, R.; Segurab, J. L.; Bäuerle, P. *Chem. Commun.* **2008**, 1320–1322.

38 (a) Fleischmann, S.; Komber, H.; Voit, B. *Macromolecules* **2008**, *41*, 5255–5264; (b) Eugene, D. M.; Grayson, S. M. *Macromolecules* **2008**, *41*, 5082–5084; (g) Rengifo, H.; Chen, L.; Grigoras, C.; Ju, J.; Koberstein, J. T. *Langmuir* **2008**, *24*, 7450–7456.

39 (a) Qin, A.; Lam, J. W. Y.; Jim, C. K. W.; Zhang, L.; Yan, J.; Haäussler, M.; Liu, J.; Dong, Y.; Liang, D.; Chen, E.; Jia, G.; Tang, B. Z. *Macromolecules* **2008**, *41*, 3808–3822.

40 Scheel, A. J.; Komber, H.; Voit, B. I. *Macromol. Rapid. Commun.* 2004, *25*, 1175–1180.

41 Che, P.; He, Y.; Wang, X. Macromolecules 2005, 38, 8657-8663.

42 Han, H.; Huang, W.; Song, C.; Xie, M.; Zhang, Y. *Macromolecules* 2009, *42*, 5036–5042.

43 Li, Z.; Yu, G.; Hu, P.; Ye, C.; Liu, Y.; Qin, J.; Li, Z. Macromolecules 2009, 42, 1589–1596.

44 Li, Z.; Yu, G.; Liu, Y.; Ye, C.; Qin, J.; Li, Z. *Macromolecules* 2009, *42*, 6463–6472.

45 Shen, X.; Liu, H.; Li, Y.; Liu, S. *Macromolecules* **2008**, *41*, 2421–2425.

46 Zhu, X.; Beginn, U.; Moller, M.; Gearba, R.; Anokhin, I. D. A. *J. Appl. Polym. Sci.* **2006**, *128*, 16928–16937.