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Hyperbranched Azo-Polymers Synthesized by Acyclic Diene Metathesis Polymerization of an AB_2 Monomer

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ABSTRACT: A novel hyperbranched azo-polymer was prepared by a ruthenium-based catalyst $RuCl_2(PCy_3)(SIMes)(CHPh)$ using acyclic diene metathesis (ADMET) polymerization of an AB_2 monomer, 4-undecylenyloxycarbonyl-4′-[bis(2-ethyl acrylate)amino]azobenzene, which was synthesized from the esterification reaction between *N,N*-bis(2-ethyl acrylate)aniline and 4-carboxy-4′-[bis(2-ethyl acrylate)amino] azobenzene. The monomer and polymer were characterized by mass spectrometer, elemental analysis, IR, UV−vis, and NMR measurements. The produced polymers have molecular weights within 5.83 and 23.5 kDa, and their polydispersity indices range from 1.73 to 1.86 by multiangle laser light scattering-gel permeation chromatography (MALLS−GPC). The hyperbranched azo-polymer underwent efficient photoisomerization from *trans* to *cis* as observation in UV−vis spectroscopy. The degree of branching (DB) was determined by using ^{1}H NMR spectroscopy and the values ranged from 0.57 to 0.45.

Introduction

Increasing attention has recently been devoted to materials containing photoresponsive units such as azobenzene because of interest in their application in fields such as photomemories,[1] optical switching,[2] optoelectronics,[3] control in liquid crystal molecules and preparing various types of dyestuff.[4] Polymers containing azobenzene-type chromophores have two important properties: a nonlinear optical property and photoresponsive *trans*−*cis* isomerization.[5] It is generally accepted that the photoinduced *trans*−*cis*−*trans* isomerization cycles of the azo chromophores play a key role in the process of forming surface-relief-gratings, which can be induced on azo polymer films by exposing to an interference pattern of Ar^+ laser beams at modest intensities.[6] Many research groups have studied the thin film preparation from azobenzene-containing polymers and their application to the optical devices because the photoinduced isomerization can cause significant bulk and surface property variation of the polymers.[7−9]

However, in the past decades, research efforts to explore new azo-polymers have predominantly focused on the linear azo-polymers with side-chain or main-chain architectures.[10−12] Recently, dendrimers containing azobenzene units in the dendritic architecture have received a great deal of attention and have been intensively designed and prepared.[13−15] In contrast to the intensive study of the azo-dendrimers, only a few hyperbranched azo-polymers have been synthesized and studied.[6,16]

Dendrimers and hyperbranched polymers are a new category of hyper-structured materials.[17] In many cases, the hyperbranched polymers are discussed as a more rapidly prepared and more economical replacement of perfect dendrimers in various applications. In contrast to their linear systems, hyperbranched polymers, as one type of dendritic polymers, have attracted increased attention with regard to design, synthesis, and functional chemistry because of their unique highly branched structures and a large number of terminal functional groups show characteristics such as their globular molecular shapes, high solubility, low solution, or melt viscosity and the feasibility to be further modified through various chemical reactions of the peripheral groups.[18−23] Although hyperbranched polymers are highly branched macromolecules and possess a less order structure, they have many similarities in structure and properties compared with dendrimers and can usually be prepared through much less time-consuming and elaborate ways such as one-pot polymerization of AB_m-type monomers (where m is generally 2 or 3).[24] The A and B functionalities of these monomers readily react with each other, but neither one reacts with itself. Compared to dendrimers, which have a well-controlled size and shape and are prepared by multistep reactions through a divergent or convergent scheme, hyperbranched polymers have less regular structures, broader molecular weight distributions, and the functional groups are distributed throughout the molecule.[19,20] Traditionally, one of the common methods of preparation of hyperbranched polymers is polycondensation of AB_m-type monomers;[25] ring-opening polymerizations and self-condensing vinyl polymerization were also used for preparing hyperbranched polymers.[26−28] However, these methods also have some drawbacks, including the need for complex monomers and harsh reaction conditions.[29] Grubbs et al. reported a relatively simple method for the synthesis of hyperbranched polymers using a new step condensation polymerization,[30] acyclic diene metathesis (ADMET) polymerization of easily synthesized monomers under mild conditions in conjunction with ruthenium-based catalysts.[31−33] The great advantage of this method is that the branched polymers are synthesized in one pot instead of tedious step-by-step process.

Recently, Wang found that hyperbranched azo-polymers can be obtained through azo-coupling reaction of an AB_2 monomer under extremely mild conditions,[12,34,35] and a variety of hyperbranched azo-polymers can be designed and prepared by lots of different ways. However, vinyl monomers cannot be polymerized by this approach. Moreover, to our knowledge, the hyperbranched azo-polymer containing a large amount of terminal

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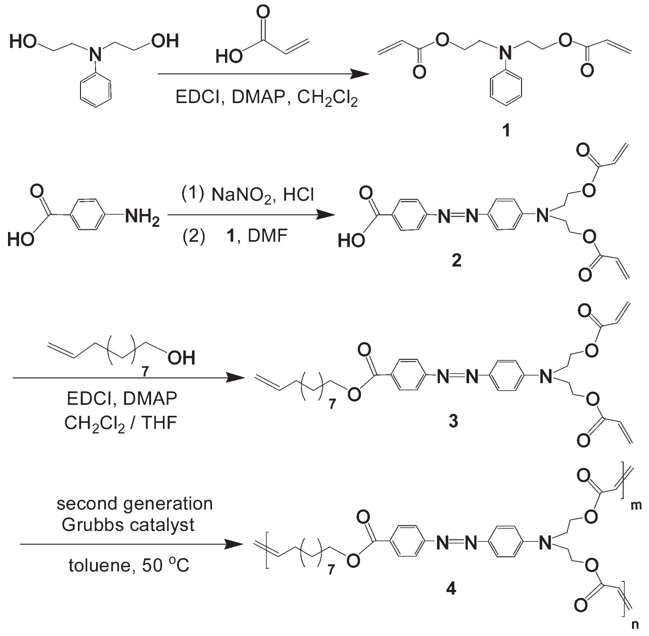
Scheme 1. Synthesis of Hyperbranched Acyclic Diene Metathesis (ADMET) Azo-Polymers[a]



[a] Key: EDCI = 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride, DMAP = 4-dimethylaminopyridine, DMF = *N*,*N*-dimethyl formamide, and THF = tetrahydrofuran.

electron-deficient and electron-sufficient alkenes groups has not been synthesized and further exploited.

Herein, we report a new synthetic protocol through ADMET polymerization of a newly designed AB_2 monomer. This type of AB_2 monomer contains azo-moiety, which functionalized with one electron-rich olefin—a terminal alkene, and two electron-poor olefins—acrylates, when treated with Grubbs' catalyst, electron-poor olefins do not homodimerize (or do so very slowly) but do participate in a secondary metathesis reaction with homodimers of more reactive olefins,[36−38] that can be polymerized into a hyperbranched structure successfully using second generation Grubbs catalyst (Scheme 1). The synthesis and characterization of monomer and the hyperbranched azo-polymer are reported in detail in this paper.

Experimental Section

Materials. Benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine)ruthenium (second generation Grubbs catalyst) (99.99%), and *N*-phenyldiethanolamine (97%) were purchased from Alfa Aesar or Aldrich and used as received without purification. Acrylic acid (98%), 4-dimethylaminopyridine (DMAP) (98%), 1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI·HCl, >99%), *p*-aminobenzoic acid (99.5%), sodium nitrite (99%), 10-undecen-1-ol (98%), and sodium acetate (99%) were purchased from Shanghai Chemical Reagents Co. and used as received without purification. Solvents were distilled over drying agents under nitrogen prior to use: *N*,*N*-dimethyl formamide (DMF) was freshly distilled and dried by sieves, methylene chloride (CH_2Cl_2) was dried over calcium hydride, and tetrahydrofuran (THF) and toluene were dried over sodium/benzophenone.

Characterization. FTIR spectra were recorded on a Nicolet Nexus 670 in the region of 4000−400 cm^{-1} using KBr pellets. UV−vis absorption spectra were measured on a UV-1900PC spectrometer. UV irradiation was carried out with 8 W UV lamp with wavelength at 365 nm. Irradiation by visible light was performed using a 23 W Philips day light bulb (>400 nm). ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded using tetramethylsilane as an internal standard in dimethyl sulfoxide-d_6 on a Bruker DPX spectrometer. Gel permeation chromatography (GPC) was performed at 45 °C at a flow rate of 1 mL/min against linear polystyrene standards (the molecular weights ranged from 10^3 to 10^6 Da) across a set of four 5 μm PL Gel columns (Polymer Laboratories) with porosities of 100, 500, and 1000 Å and Mixed C. The eluting material was observed with a dual UV (254 nm) and refractive index detection system. Light scattering measurements were performed on a DAWN EOS laser photometer (30 mW GaAs linearly polarized laser, 690 nm) and an Optilab DSP interferometer refractometer (690 nm, Wyatt Technology) in GPC mode with the Debye fit method for data analysis. GC/MS measurements were performed with a Varian Saturn 2100 GC/MS system with GC-3900 using a VF-5 MS, 30 m × 0.25 mm × 0.25 μm diffused silica capillary column. Elemental analysis (EA) was conducted with an Elementar vario EL.

Polymerizations were carried out in Schlenk tubes using of a nitrogen flow to drive off the ethylene condensate for ADMET.

Synthesis of *N*,*N*-Bis(2-ethyl acrylate)aniline (1). To a round-bottom flask were added *N*-phenyldiethanolamine (5.43 g, 30 mmol), acrylic acid (6.15 g, 85 mmol), and DMAP (0.88 g, 7.2 mmol). These materials were dissolved in 100 mL of dry CH_2Cl_2 and cooled to 0 °C, EDCI (13.8 g, 72 mmol) was then added to this solution, and the reaction mixture was warmed to room temperature and subsequently stirred for 72 h under nitrogen flow. After repeated washing with deionized water, the organic layer was dried over anhydrous Na_2SO_4. Solvent was then removed under reduced pressure and the crude product was purified by silica gel chromatography eluted with methylene chloride/petroleum ether (18/1) to give a viscous colorless liquid **1** (6.54 g, 75.4% yield). ^1H NMR (DMSO-d_6): δ (ppm) 7.19−7.16 (m, 2H, *m*-Ar*H*), 6.82−6.80 (d, 2H, *o*-Ar*H*), 6.64−6.62 (m, 1H, *p*-Ar*H*), 6.33−6.30 (d, 2H, OCOCH=C*H*), 6.19−6.15 (m, 2H, OCOC*H*=CH), 5.96−5.93 (d, 2H, OCOCH=C*H*), 4.27−4.25 (m, 4H, C*H*$_2$−O), 3.67−3.65 (m, 4H, N−C*H*$_2$). ^{13}C NMR (DMSO-d_6): δ (ppm) 165.45 (CH$_2$O*C*O), 147.19 (Ar*C*−N), 131.69 (OCOCH=*C*H), 129.13 (*m*-Ar*C*), 128.09 (OCO*C*H=CH), 116.16 (*o*-Ar*C*), 111.82 (*p*-Ar*C*), 61.40 (*C*H$_2$OCO), 48.84 (N−*C*H$_2$). GC: single peak observed at the retention time of 14.4 min. EI/MS: calcd for $C_{16}H_{19}NO_4$, 288.9; found, 288.9.

Synthesis of 4-Carboxy-4′-[bis(2-ethyl acrylate)amino]azobenzene (2). A solution of sodium nitrite (1.24 g, 18 mmol) in water (6 mL) was added dropwise to the solution of *p*-aminobenzoic acid (2.47 g, 18 mmol) in 20 wt % aqueous HCl (10 mL) at 0 °C and stirred for 1 h. A cooled solution of **1** (4.34 g, 15 mmol) in DMF (40 mL) was then added dropwise to the former solution at 0 °C and stirred further for 4 h. The resulting mixture was poured into water and the crude product was precipitated out by neutralizing the reaction mixture with sodium acetate solution, and further purified by recrystallization from ethanol to afford a red crystalline powder **2** (5.64 g, 86.1% yield). IR, ν (cm^{-1}): 2921, 2850 (CH$_2$, stretch), 1725 (ester C=O, stretch), 1679 (aromatic COOH, stretch), 1597, 1512 (aromatic C=C, stretch), 1397 (C−N, stretch), 1274, 1186, 1133 (C−O, stretch), 1065, 987 (=C−H, bend). ^1H NMR (DMSO-d_6): δ (ppm) 13.07 (s, 1H, COO*H*), 8.10 (d, 2H, *o*-Ar*H*−COOH), 7.85−7.81 (m, 4H, *o*-Ar*H*−*N*=N−Ar*H*), 7.03−7.01 (d, 2H, *m*-ArH−*N*=N−Ar*H*-N), 6.34−6.30 (d, 2H, OCOCH=C*H*), 6.19−6.13 (m, 2H, OCOC*H*=CH), 5.96−5.94 (d, 2H, OCOCH=C*H*), 4.36−4.33 (m, 4H, C*H*$_2$−O), 3.84−3.82 (m, 4H, NC*H*$_2$). ^{13}C NMR (DMSO-d_6): δ (ppm) 166.88 (*C*OOH), 165.44 (CH$_2$O*C*O), 154.97 (Ar*C*−*N*=N−ArC), 151.04 (ArC−*N*=N−Ar*C*−N), 143.08 (ArC−*N*=N−Ar*C*), 131.93 (HOOC−Ar*C*), 131.09 (OCOCH=*C*H), 130.52 (*m*-Ar*C*−*N*=N−ArC), 128.03 (OCO*C*H=CH), 125.26 (*m*-ArC−*N*=N−Ar*C*), 121.82 (*m*-ArC−*N*=N−Ar*C*), 111.93 (*p*-ArC−*N*=N−Ar*C*), 61.41 (CH$_2$*C*H$_2$OCO), 48.86 (*C*H$_2$CH$_2$O-CO). Anal. Calcd: C, 63.150; H, 5.299; N, 9.606. Found: C, 63.175; H, 5.393; N, 9.532.

Synthesis of 4-Undecylenyloxycarbonyl-4′-[bis(2-ethyl acrylate)amino]azobenzene (3). 10-Undecen-1-ol (2.04 g, 12 mmol), **2** (4.37 g, 10 mmol), DMAP (0.15 g, 1.2 mmol), CH_2Cl_2 (60 mL), and THF (10 mL) were charged into a 150 mL round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere, and the mixture was stirred at 0 °C for 15 min. EDCI (2.23 g, 12 mmol) was then added to the former solution, and stirred for 3 days after the solution warmed to room temperature. The resulting solution was washed three times with deionized water (3 × 80 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was then evaporated, and the crude product was purified by silica gel chromatography eluted with methylene chloride/petroleum ether (30/1) to give a viscous dark red liquid **3** (5.32 g, 90.3% yield). IR, ν (cm^{-1}): 2924, 2852 (CH_2, stretch), 1725 (ester C═O, stretch), 1599, 1513 (aromatic C═C, stretch), 1407 (C−N, stretch), 1272, 1183, 1139 (C−O, stretch), 1095, 986 (═C−H, bend). ^{1}H NMR (DMSO-d_6): δ (ppm) 8.10−8.08 (d, 2H, *o*-Ar*H*−OCO), 7.88−7.81 (m, 4H, *o*-Ar*H*−*N*═N−Ar*H*), 7.03−7.01 (d, 2H, *m*-ArH−*N*═N−Ar*H*−N), 6.33−6.29 (d, 2H, OCOCH═C*H*), 6.18−6.13 (m, 2H, OCOC*H*═CH), 5.96−5.93 (d, 2H, OCOCH═C*H*), 5.77 (m, 1H, CH═C*H*CH$_2$), 5.00−4.91 (m, 2H, C*H*═CHCH$_2$), 4.36−4.34 (m, 4H, C*H*$_2$OCOCH═CH), 4.33−4.27 (m, 2H, C*H*$_2$OCO−ArH), 3.84−3.81 (m, 4H, NC*H*$_2$), 2.00−1.97 (m, 2H, CH═CHC*H*$_2$), 1.73−1.70 (m, 2H, C*H*$_2$CH$_2$OCO), 1.42−1.38 (m, 2H, C*H*$_2$CH$_2$CH$_2$OOC), 1.33−1.26 (m, 10H, C*H*$_2$). ^{13}C NMR (DMSO-d_6): δ (ppm) 165.39 (CH$_2$O*C*OCH═CH), 165.28 (CH$_2$O*C*O−Ar), 155.14 (Ar−*CN*═NAr−C), 151.11 (Ar−CN═NAr−*C*N), 143.09 (Ar−CN═NAr−*C*), 138.78 (CH═*C*HCH$_2$), 131.86 (CH$_2$OCOAr−*C*), 130.29 (CH$_2$OCOCH═*C*H), 130.06 (*m*-Ar−*CN*═NAr−C), 128.00 (CH$_2$OCO*C*H═CH), 125.27 (*m*-Ar−CN═NAr−*C*), 121.91 (*m*-Ar−CN═NAr−*C*), 114.55 (*C*H═CH−CH$_2$), 111.92 (*p*-Ar−CN═NAr−*C*), 64.81 (*C*H$_2$OCOAr−C), 61.38 (*C*H$_2$OCOCH═CH), 48.84 (*C*H$_2$CH$_2$OCOCH═CH), 33.13 (CH═CH*C*H$_2$), 30.63 (*C*H$_2$CH$_2$-OCO−Ar), 28.82−28.11 (*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$), 25.42 (CH$_2$-CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$). Anal. Calcd: C, 69.247; H, 7.349; N, 7.125. Found: C,69.370; H, 7.286; N, 7.181.

Representative Polymerization Procedure. In a nitrogen-filled Schlenk tube, a solution of second generation Grubbs catalyst (1.7 mg, 2.0 μmol) in 0.5 mL of degassed toluene with three freeze-vacuum-thaw cycles was added to a solution of monomer **3** (235.6 mg, 0.4 mmol) in 0.5 mL of toluene degassed with the same procedure. After the reaction mixture was stirred at 50 °C for 1−6 days, the polymerization was quenched by adding ethyl vinyl ether with stirring for 30 min. The solution was precipitated into an excess of methanol, and the precipitate was isolated by filtration, dried under vacuum for 24 h to give the polymer as a dark-red semisolid **4**. IR, ν (cm^{-1}): 2920, 2851 (CH_2, stretch), 1722 (ester C═O, stretch), 1598, 1512 (aromatic C═C, stretch), 1393 (C−N, stretch), 1270, 1181, 1137 (C−O, stretch), 1094, 986 (═C−H, bend). ^{1}H NMR ($CDCl_3$): 8.15−8.13 (d, *o*-Ar*H*−OCO), 7.90−7.85 (m, *o*-Ar*H*−*N*═N−Ar*H*), 6.99−6.94 (m, OCOCH═C*H*), 6.88−6.87 (d, *m*-ArH-*N* = N−Ar*H*-N), 6.43−6.39 (d, OCOCH = *CH*), 6.15−6.12 (m, OCOC*H* = CH), 5.87−5.79 (d, OCOCH═C*H*), 4.39 (m, C*H*$_2$OCOCH═CH), 4.36−4.32 (m, C*H*$_2$OCO−ArH), 3.78 (m, NC*H*$_2$), 2.18−2.16 (m, CH═CHC*H*$_2$), 1.78 (m, C*H*$_2$CH$_2$OCO), 1.44−1.43 (m, C*H*$_2$-CH$_2$CH$_2$OOC), 1.30−1.27 (m, C*H*$_2$). MALLS−GPC: M_n = 5830, $M_w/M_n = 1.73$ for 1 day; $M_n = 14700$, $M_w/M_n = 1.75$ for 3 days; $M_n = 23500$, $M_w/M_n = 1.86$ for 6 days.

Results and Discussion

Preparation of *N,N*-Bis(2-ethyl acrylate)aniline. The AB_2 type monomer was successfully prepared by a three-step technique. As the first step, *N,N*-bis(2-ethyl acrylate)aniline, **1** was synthesized from a reaction of *N*-phenyldiethanolamine with acrylic acid catalyzed by DMAP in CH_2Cl_2 at room temperature (Scheme 1). In order to realize double substitution of dihydroxyl groups by esterification, excess of acrylic acid is necessary to have dihydroxyl completely consumed, and the suitable ratio of *N*-phenyldiethanolamine to acrylic acid was 1:1.5. Under this condition, thin layer chromatography analysis showed the expected product was dominant in the reaction mixture. The crude oil was purified by column chromatography to provide pure product with good yield of 75.4%.

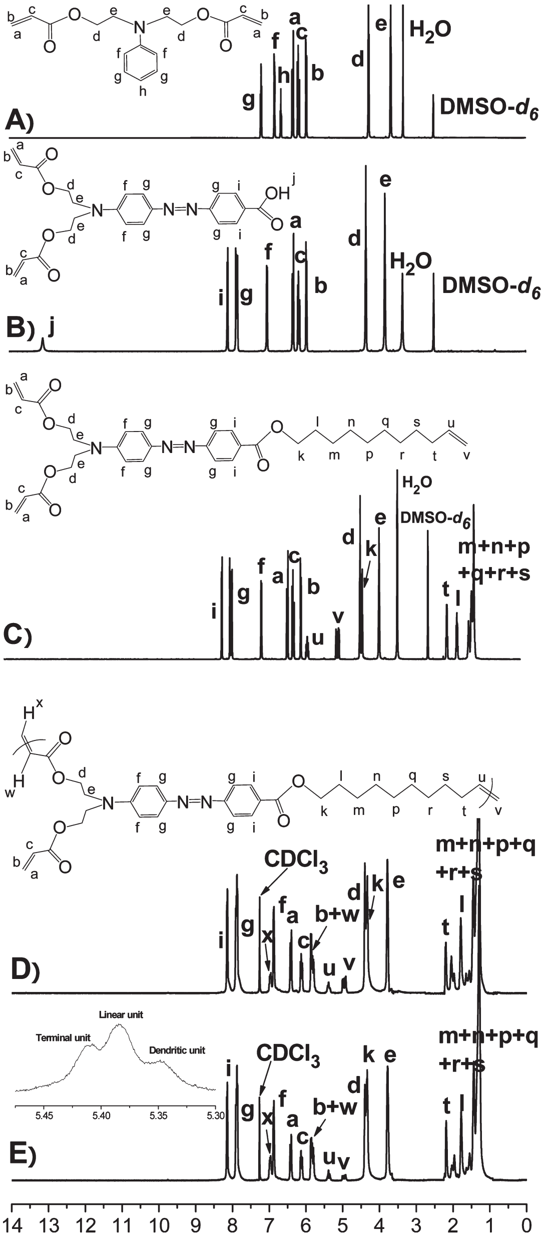


Figure 1. ^{1}H NMR spectra for (A) *N,N*-bis(2-ethyl acrylate)aniline, (B) 4-carboxy-4′-[bis(2-ethyl acrylate)amino]azobenzene, (C) AB_2 monomer 4- undecylenyloxycarbonyl-4′-[bis(2-ethyl acrylate)amino]azobenzene, (D) hyperbranched azo-polymer for 3 days, and (E) hyperbranched azo-polymer for 6 days.

The ^{1}H NMR spectrum (Figure 1A) showed the resonance signals of C*H*$_2$═CHOCO− protons (*a*, *b*) at 6.33 ppm, 5.96 ppm and CH$_2$═C*H*OCO− protons (*c*) at 6.19 ppm. Furthermore, the molecular weight (M_n = 288.9) of **1** from MS analysis was in good accordance with the calculated value, and the product also has a high purity estimated from the single peak of GC chromatogram. All of these points affirmed the successful preparation of **1** with the expected structures by esterification.

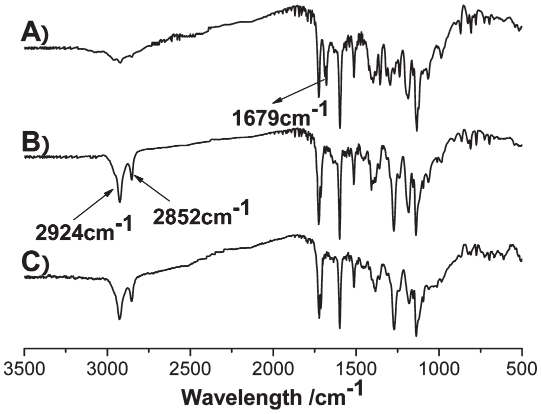


Figure 2. FITR spectra for (A) azobenzene chromophore, 4-carboxy-4′-[bis(2-ethyl acrylate)amino]azobenzene, (B) AB_2 monomer 4- undecylenyloxycarbonyl-4′-[bis(2-ethyl acrylate)amino]azobenzene, and (C) hyperbranched azo-polymer.

Synthesis of Azobenzene Chromophore. Azobenzene chromophore, **2** was synthesized by a similar method to that reported by Silong et al.[39] The azo moiety was prepared from the starting material *p*-aminobenzoic acid, in which the amino group was diazoted by sodium nitrite, and then the diazonium salt was coupled with **1** to produce the compound **2**. The chemical structure of product was confirmed by elemental analysis, FTIR, and ^{1}H NMR spectroscopy. Figure 1B shows the ^{1}H NMR spectrum of monomer **2**, we can observe the appearance of two groups of new resonance peaks at *j* (13.07 ppm) and *i* (8.10 ppm), which can be ascribed to the protons of terminal carboxyl and benzene ring. As compared to that of **1**, it was a clearly observation that a clean chemical shift of the peaks of both *g* and *f* initially at 7.19 and 6.82 ppm in Figure 1A to the higher field at 7.85 and 7.03 ppm for protons of benzene ring after forming the azo-linkages in Figure 1B. Furthermore, peak *h* initially at 6.64 ppm in Figure 1A disappeared in Figure 1B, while the signals of *a*, *b*, *c*, *d*, and *e* were still observed, which meant azobenzene was virtually formed. In the IR spectrum of the chromophore **2** in Figure 2A, the absorption bands characteristic peaks at 2921, 1725, 1697, 1597, 1512, 1274, 1186, 1133, 1065, and 987 cm^{-1} were attributed to the stretching vibration of unsaturated C=C−H and saturated C−H, ester (C=O), carboxyl, azobenzene, −C−O, and out-of-plane bending vibrations of the C−H bond of the −C=CH_2 group, respectively, which further confirmed the successful attachment of azobenzene groups to **1** backbone. All of these points also assured that the azobenzene chromophore has been successfully prepared.

Synthesis of Azobenzene AB_2 Monomer. Monomer **3** was prepared by a similar esterification reaction, as described previously (Scheme 1). The esterification reaction of **2** with an excess of 10-undecen-1-ol was carried out at room temperature to produce AB_2 monomer **3**. ^{1}H NMR spectrum and the corresponding peak assignments of **3** were shown in Figure 1C. After **2** reacted with the alcohol, resonance signals of terminal carboxyl protons *j* (13.07 ppm) neighboring to benzene ring completely disappeared, the resonance signals of *u* (5.77 ppm) and *v* (5.00−4.91 ppm) were newly formed. Moreover, resonance signals of methylene protons *t* (2.00 ppm), *l* (1.73 ppm) and *m*−*s* (1.41−1.26 ppm) can be also clearly observed, which correspond to the chemical structure of the alcohol. This strongly suggests complete transformation of terminal carboxyl into terminal double bond (CH_2=CH−). When compared the IR spectrum of the chromophore **3** with **2**, we can also clearly observe in Figure 2B that the absorption bands at 1725, 1599, and 1513 cm^{-1} exhibited no significant change, while a strong absorption peak at 1679 cm^{-1} disappeared, and some middle strong sharp peaks in region of 2850−2925 cm^{-1} strengthened in evidence, which contributed by the aliphatic hydrocarbons stretching vibration of 10-undecen-1-ol.

Preparation of Hyperbranched Azo-Polymers. Hyperbranched azo-polymers, **4**, were synthesized by ADMET in conventional reaction conditions. The polymer was precipitated to an excess of methanol to provide pure product. The polymerization of AB_2 monomer is easily monitored by ^{1}H NMR spectroscopy.[40,41] It is obvious that the curves of polymers are similar with their monomer as their structures are alike. For comparison, we also investigated the different of polymerization time. However, the length of the catalyst's lifetime in the reaction solution limits the effectiveness of prolonging the polymerization time past 3 days, so a fresh batch of 0.25% mol equiv of the catalyst is then added to the reaction vessel at about 3 day intervals.[30] Parts D and E of Figure 1 show the ^{1}H NMR spectra of the resulting polymer **4** with the extending of the polymerization time from 3 to 6 days. It can be seen that the terminal olefins (*v*) almost completely disappear after 6 days polymerization in Figure 1E but still clearly detect when polymerized for 3 days in Figure 1D. Moreover, as expected, a new peak (*x*) appears at 6.96 ppm due to formation of internal acrylates (AB olefins), and importantly in Figure 1E, the integration area ratio of *x* and the remaining unreacted acrylate peak *c* characteristic resonances of 1:1 was well agreed with the fact that there are twice as many B groups as A groups in an AB_2 monomer but the ratio of 1:2 in Figure 1D, which indicated that polymerization proceeds to completion in Figure 1E, consuming almost all of the terminal aliphatic alkenes, and there are half of the free acrylate groups left in the final polymer; however, almost consuming half of the terminal aliphatic alkenes in Figure 1D. These results implied that the conversion of monomer increased with longer polymerization time.

GPC is well-known to determine the molecular weight and molecular weight distribution for linear polymers by using calibration with linear polystyrene. However, for hyperbranched polymers, its size is smaller than that of linear ones with same molecular weight.[42] Therefore, we employed multiangle laser light scattering (MALLS) as an absolute molecular weight characterization method to further characterize the hyperbranched polymers. The typical polymerization results are summarized in Table 1. Indeed, the MALLS-derived weight average molecular weights (M_w) of hyperbranched azo-polymer **4** were significantly higher than the GPC values based on polystyrene calibration.

Table 1. Characteristics of Hyperbranched Azo-Polymers by ADMET Using Second Generation Grubbs Catalyst[a]

entry	*t* (day)	conversion (%)[b]	M_w (kDa)[c]	M_n (kDa)[c]	PDI[c]	M_w (kDa)[d]	DB[e]
1	1	76	7.72	5.83	1.73	3.34	0.57
2	3	75	25.8	14.7	1.75	15.9	0.52
3	6	78	43.6	23.5	1.86	20.2	0.45

[a] Polymerization conditions: $[M]_0 = 0.4$ mol/L, polymerization temperature = 50 °C, toluene = 1.0 mL, [second generation Grubbs catalyst] = 2.0×10^{-3} mol/L. [b] Obtained gravimetrically after purification from the dried polymer. [c] Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersed index (PDI) were calculated from multiangle laser light scattering. [d] Determined by gel permeation chromatography in THF relative to monodispersed polystyrene standards. [e] The degree of branching (DB) was calculated from integration of ^{1}H NMR spectrum.

This is consistent with the general trends for hyperbranched polymers. It was also shown that the resulting polymer has a moderate molecular weight from 5.83 kDa to 23.5 kDa with reasonable lower polydispersed index (PDI) ranging from 1.73 to 1.86, Additionally, the MALLS−GPC traces of the hyperbranched polymers obtained from different polymerization time are shown in Figure 3. With the progress of polymerization, the elution curves are gradually shifted to higher molecular weight region and PDI also becomes more wide (from curve A to C), indicating the increasing of hyperbranched chain length. As expected, longer polymerization times result in higher molecular weights, this is in accord with that of NMR measurement.

The IR spectrum for hyperbranched azo-polymers is shown in Figure 2C. The absorption bands are almost the same as **3**. Therefore, we concluded that ADMET hyperbranched polymer has a similar backbone structure to azobenzene AB$_2$ monomer.

Degree of Branching (DB). DB is one of the important molecular parameter to evaluate the branching density of hyperbranched polymers and to distinguish them from other types of macromolecules. The possible units present in a repeat unit of hyperbranched polymer are dendritic (D), linear (L), and terminal (T) units, and the distributions of these three units play a prominent role in altering the properties of hyperbranched polymers. Generally, DB is defined as the sum of dendritic and terminal units relative to the total number of units, i.e. DB = (D + T)/(D + L + T).[43] There are two methods—the Frechet method[44] and the Frey method[45]—available for the determination of DB. Thus, we determined the DB of hyperbranched azo-polymers by Frechet method using ^{1}H NMR spectra of polymers. D, T, and L units which mimic exactly the units presented in the hyperbranched azo-polymer were described in Scheme 2.

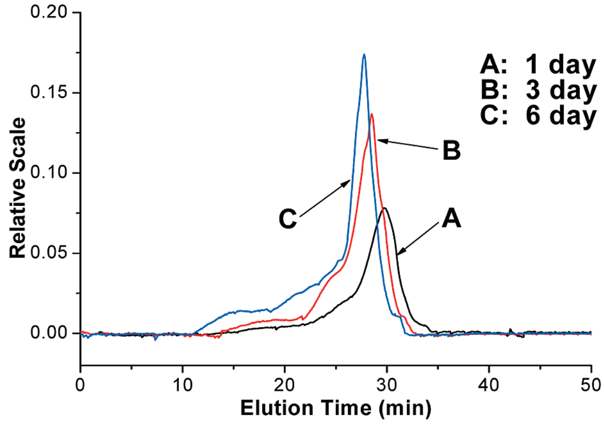


Figure 3. Representative multiangle laser light scattering-gel permeation chromatography (MALLS−GPC) traces for polymer **4**.

It was possible to assign peaks for protons of individual unit clearly in the alkene regions. The enlarged ^{1}H NMR spectrum of polymer in Figure 1E showed three discrete signals for $-CH{=}CH_2$ protons at 5.41, 5.38, and 5.34 ppm, which are corresponding to the protons in T, L, and D units, respectively. On the basis of the mole fractions of D, L, and T units obtained from the integration values, the DB values were calculated and given in Table 1. The results reveal that the DB is high for low molecular weight polymer and is low for high molecular weight polymer, ranging from 0.45 to 0.57, which is in good agreement with the ideal DB value of 0.5.[46] The high DB value indicates that the low molecular weight polymer may have more number of terminal units and less number of linear units.

Photoisomerization in Solution. It is well-known that polymers containing azobenzene-type chromophores have the *cis* and *trans* isomers. Generally, the *cis* form of the azobenzene molecule is thermodynamically less stable than the *trans*

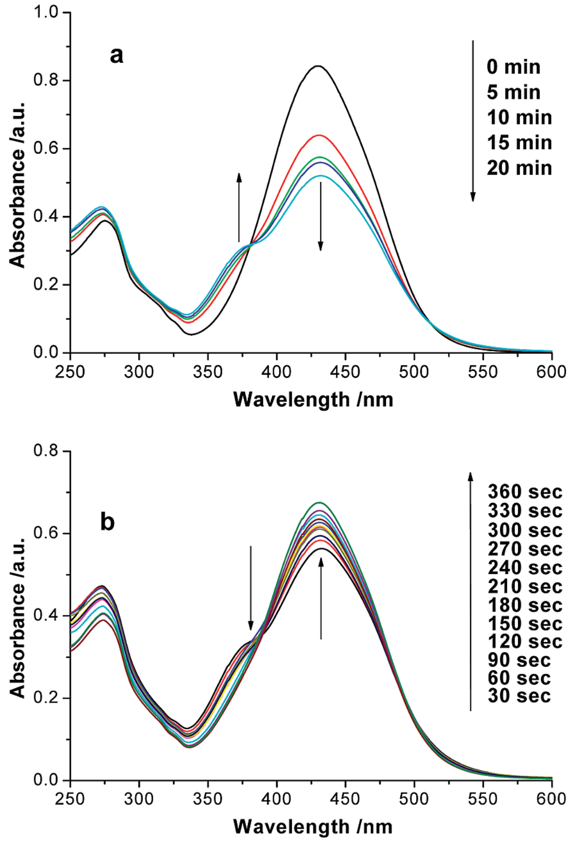
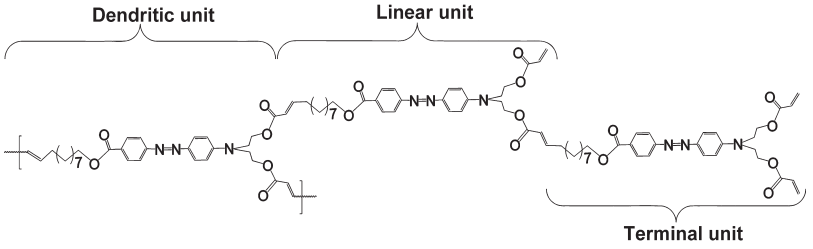


Figure 4. UV−vis spectra of hyperbranched azo-polymer in tetrahydrofuran (THF) solution with a concentration of 20 μg/mL. (a) Absorbance changes with visible light exposure time. At exposure time of zero (the highest curve), the sample has been in dark for 48 h. (b) Absorbance of the sample that has reached the photostationary state in part a changes with UV irradiation (365 nm) time.

Scheme 2. Three Representative Units of Hyperbranched Azo-Polymer 4



form. Therefore, when there is a lack of the actinic light, the *cis* form obtained by photoisomerization will change into the *trans* form. However, sometimes the *cis* isomers of azobenzenes are thermodynamically stable, this kind of reverse cases also have been reported in literature.[47−50]

UV−vis sprectroscopy was primarily used to characterize the process of photoisomerization of the azobenzene moieties. The photoresponsive properties of the hyperbranched azo-polymer were observed in dilute THF solutions at selected time intervals in this article. As illustrated by the UV−vis spectra in Figure 4, the hyperbranched azo-polymer in THF solutions was exposured to varying conditions of UV irradiation or visible light. The absorption band at about 381 nm is attributed to the $\pi \rightarrow \pi^*$ transition in *trans* isomer and the band at 431.5 nm to the $n \rightarrow \pi^*$ transition in *cis* isomer. In Figure 4a, the sample solution was stored in the dark for 48 h to ensure the presence of pure *cis* isomer. However, when exposuring to visible light, absorption of the $n \rightarrow \pi^*$ band at 431.5 nm progressively decreased and absorption of the $\pi \rightarrow \pi^*$ band at 381 nm increased with irradiation time, indicating a photochemical conversion from *cis* to *trans* isomer configuration, and the existence of a photostationary state after about 20 min of irradiation because there were no further significant changes in the spectra.

It has also reported that almost all the azobenzene dendrons showed more conversion from the *trans* isomer to *cis* isomer at the photostationary state, and the *cis* form of the azobenzene dendron was more stable than the *trans* form in the dark, but showed very short photoactivated lifetime (2 min) of *cis* form.[13] In this study, when irradiating the diluted solution by UV light of 365 nm, there is the same isomerization as the azobenzene dendron as shown in Figure 4b, the absorption at 381 nm decreases, and that at 431.5 nm increases simultaneously, with a photostationary state reached after about 5 min. The sample could also reach its initial state as the *cis* form in 48 h at darkness though a thermal isomerization process. Then we characterized the UV isomerization efficiency of azo-polymer by calculating the ratio of $A^{trans \rightarrow cis}/A_0$, which denote the absorbance at photostationary state of UV induced *trans* to *cis* isomerization process. A_0 is the absorbance maximum of the sample in 48 h in darkness.[13] For this hyperbranched azo-polymer, the photoisomerization efficiency was 0.84, which indicated that most of azo group undergo isomerization process. All these results show that this kind of azobenzene-functionalized hyperbranched polymer can also undergo *trans* to *cis* photoisomerization efficiently, while keep long photoactivated lifetime of *cis* form, which resulting from the limitation of *trans-cis* configuration conversion in this main-chain hyperbranched azobenzene polymer and therefore it needs more transition times.

Conclusion

Hyperbranched azo-polymer was successfully prepared through ADMET polymerization using second generation Grubbs catalyst under conventional conditions based on a newly azo moiety-contained AB_2 monomer, which functionalized with one electron-rich terminal alkene, and two electron-poor acrylates. The structure of hyperbranched azo-polymer was confirmed by IR, UV−vis, and NMR measurements. The results of MALLS−GPC analysis showed the produced polymer with moderate molecular weight and relatively narrow molecular weight distribution. The photoisomerization of hyperbranched azo-polymer was detected by UV−vis technique and the DB values were also calculated using ^{1}H NMR spectroscopy. The synthetic scheme demonstrated in this work is a feasible way to prepare an AB_2 type of hyperbranched azo-polymer.

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