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Synthesis and characterization of hyperbranched azobenzene-containing polymers via self-condensing atom transfer radical polymerization and copolymerization

Ming Jin, Ran Lu*, Chunyan Bao, Tinghua Xu, Yingying Zhao

College of Chemistry, 119 Jiefang Raod, Jilin University, Chang Chun 130023, China

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Abstract

We report on the synthesis of an azobenzene-containing inimer 6-{4-[4-(2-(2-bromoisobutyryloxy)hexyloxy)phenylazo]phenoxy}hexyl methacrylate (**I**) and used it to prepare hyperbranched homopolymer and copolymers by self-condensing vinyl polymerization (SCVP) and copolymerization (SCVCP) with its precursor 6-{4-[4-(6-hydroxyhexyloxy)phenylazo]phenoxy}hexyl methacrylate (**M**) using atom transfer radical polymerization (ATRP). Depending on the comonomer ratio, $\gamma = [M]_0/[I]_0$, branched polymethacrylates with number-average weights between 8000 and 20,000 and degree of branching (DB) between 0.08 and 0.49 were obtained by SCVCP, as evidenced by GPC and ^{1}H NMR analysis. In addition, the photochemical properties of the polymers were also studied by UV–vis spectra and found the structure of polymers affect obviously the *trans–cis* isomerization properties of the branched polymers.

Keywords: Atom transfer radical polymerization; Azobenzene; Hyperbranched

1. Introduction

Dendritic polymers including dendrimers and hyperbranched polymers have become a major research interest in polymer science [1–4]. Especially, dendrimers with azo chromophores in the dendritic architecture have been designed and prepared recently [5–11]. Because they could be used in the fields of optical data storage, nonlinear optical materials, holographic memories; etc. [12–15]. The highly branched structures lead to their globular, void-containing shapes, high solubility, and low solution or melt viscosity compared to linear analogues. 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.

Traditionally, hyperbranched polymers have been prepared by polycondensation reactions of AB_2 monomer [16]. For example, Wang et al. synthesized hyperbranched azobenzene-containing polymers with ester exchange reaction [17,18]. However, vinyl monomers cannot be polymerized by this approach. This drawback was overcome by self-condensing vinyl polymerization (SCVP) of initiator-monomer having the general structure AB^*, where A stands for a double bond and B^* represents an initiating group [19]. Thus, these molecules combine features of an initiator and a monomer and have therefore been named 'inimer' [20–22]. This approach has been applied to various types of living polymerization, i.e. cationic [1], ATRP [23,24], ring-opening polymerization [25]. In addition, this approach has been extended to synthesize other hyperbranched copolymers with the self-condensing vinyl copolymerization (SCVCP) of a vinyl monomer M and an 'inimer' AB^*. Müller et al. have calculated analytically the kinetics, molecular weight averages and the average degree of branching for SCVCP and discussed the gained randomly branched architecture as a function of the comonomer ratio, γ, and the comonomer-to-catalyst ratio, μ, in the feed [26]. Moreover, the effects of the ligand used to complex copper ions, solvent, and temperature on the resulting molecular parameters were also studied by them. It was found that

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* Corresponding author. Tel.: +86-4318499179; fax: +86-4318949334. *E-mail address:* luran@mail.jlu.edu.cn (R. Lu).

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control of the structures of the branched polymers in terms of molecular weight, polydispersity, degree of branching, and comonomer composition plays a crucial role in manipulation of the properties of polymers [3].

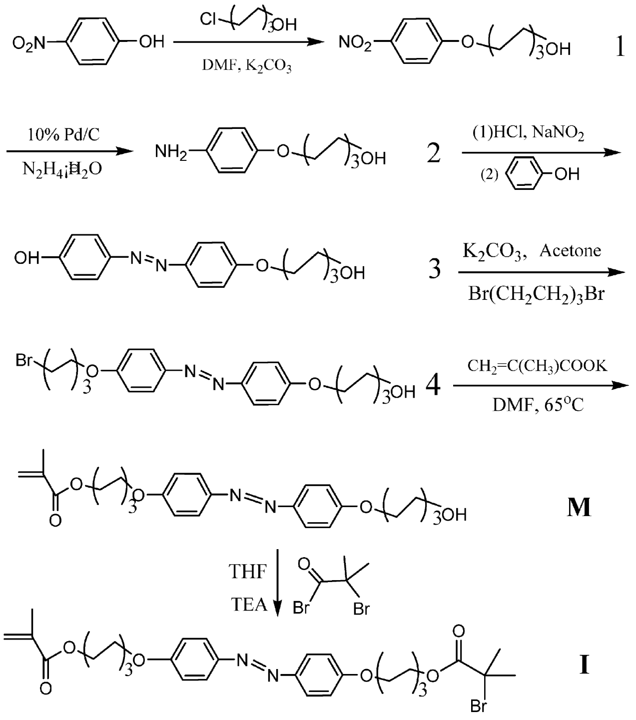
This paper reports on the preparation of an azo-containing inimer and used it to synthesize a series of branched polymethacrylates by SCVP and SCVCP with its precursor via ATRP using the CuBr/ligand catalyst system. The great advantage of this method is that the branched polymers are synthesized in one pot instead of tedious step-by-step process. Moreover, the gained polymers have narrow polydispersity index in the range of 1.20–1.46 and their degree of branching can be modified easily by a suitable choice of the comonomer ratio in the feed. In this study, we also discussed the photo-responsive properties of resulting homopolymer and copolymers.

2. Experimental section

2.1. Materials and methods

^{1}H nuclear magnetic resonance (NMR) spectra of monomer and polymers in $CDCl_3$ were obtained on a Varian 300 MHz FT-NMR spectrometer. Infrared spectra were measured using a Nicolet-360 FT-IR spectrometer by incorporating samples in KBr disks. The UV–vis absorption spectra of the polymers in THF solutions were determined on a Shimadzu-1601 spectrophotometer. *Trans–cis* photo-isomerizations of azobenzene units were carried out by using an Hg lamp with filters. The molecular weights were determined by gel permeation chromatography (GPC) utilizing waters 510 pump and Model 410 differential refractometer. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 ml/min.

Anisole as the solvent for solution polymerization was purified by distillation from sodium with benzophenone. Catalyst CuBr (Aldrich) was washed successively with acetic acid and ether, then dried, and stored under nitrogen. 2-Bromo-2-methylpropionyl bromide and the ligand 1, 1, 4, 7, 10, 10-hexamethyltriethylenetetramine (HMTETA, Aldrich) were used as received without further purification. All of the other chemicals were obtained commercially and were used as received unless otherwise stated. The synthetic procedure used in the preparation of the inimer was described in Scheme 1.



Scheme 1. The synthetic route of inimer and monomer.

2.2. Synthesis of inimer

2.2.1. Synthesis of 6-(4-Nitrophenoxy)hexanol (*1*)

4-Nitrophenol (0.1 mol) and an excess amount of 6-chloro-hexanol (0.3 mol) and potassium carbonate (0.15 mol) were added to a 250 ml of round-bottom flask equipped with reflux condenser. DMF (100 ml) was added, and the mixture was heated to 110 °C for 8 h. Then the mixture was poured hot into water (500 ml). After the product was collected by filtration and washed with water, it was dried in vacuum and recrystallized from ethyl acetate. Yield is 90%. ^{1}H NMR ($CDCl_3$, ppm): 8.150 (d, 2H, aromatic), 6.913 (d, 2H, aromatic), 4.052 (t, 2H, OCH_2), 3.625 (t, 2H, CH_2OH), 1.421–1.892 (m, 8H, aliphatic). IR (KBr): 3200–3500 (OH), 1650, 1360 (NO_2) cm^{-1}.

2.2.2. Synthesis of compound 4-(6-hydroxyhexyloxy) aniline (*2*)

0.1 mol of compound **1** and 0.3 g of Pd/C (10%) were added in 100 ml ethanol. Then 30 ml of hydrazine hydrate was dropwise added to the mixture under refluxing within 1 h. After 2 h, the catalyst was filtered hot. The filtrate was concentrated to half, then cold to room temperature; the precipitation was filtered and dried in vacuum to give yield (65%) of white product. ^{1}H NMR ($CDCl_3$, ppm): 6.720 (d, 2H, aromatic), 6.646 (d, 2H, aromatic), 3.878 (t, 2H, OCH_2), 3.636 (t, 2H, CH_2OH), 1.750 (m, 2H, aliphatic), 1.563 (m, 2H, aliphatic), 1.441 (m, 4H, aliphatic). IR (KBr): 3365 (OH), 3200 (NH_2) cm^{-1}.

2.2.3. Synthesis of (6-hydroxyhexyloxy) azobenzene (*3*)

Compound **3** was synthesized by using the diazonium salt of compound **2** coupled with phenol at 0 °C. ^{1}H NMR, (d_6-acetone, ppm): 9.342 (s, 1H, OH), 7.886 (d, 2H, aromatic), 7.806 (d, 2H, aromatic), 7.115 (d, 2H, aromatic), 6.977 (d, 2H, aromatic), 3.998 (t, 2H, OCH_2), 3.662 (t, 2H, CH_2OH), 1.763 (m, 2H, aliphatic), 1.581(m, 2H, aliphatic), 1.461 (m, 4H, aliphatic). IR (KBr): 3300 (OH), 2935, 2865 (CH_2), 1600, 840 (phenyl) cm^{-1}.

*2.2.4. Synthesis of 4-(6-bromohexyloxy)-4′-(6-hydroxyhexyloxy) azobenzene (**4**)*

It was obtained by reaction of compound **3** with an excessive amount 1,6-dibromohexane in the presence of anhydrous K_2CO_3 and KI in dry acetone with 85% yield. ^{1}H NMR, ($CDCl_3$, ppm): δ, 7.851 (d, 4H, aromatic), 6.995 (d, 4H, aromatic), 4.030 (t, 4H, OCH_2), 3.665 (t, 2H, CH_2OH), 3.431 (t, 2H, CH_2Br), 1.639–1.906 (m, 8H, aliphatic), 1.466–1.617 (m, 8H, aliphatic). IR (KBr): 3304 (OH), 2937, 2862 (CH_2), 1601, 1496, 843 (phenyl) cm^{-1}.

*2.2.5. 6-[6-(Methacryloyloxy)hexyloxy]-6′-(hydroxyhexyloxy)azobenzene (**M**)*

It was gained by esterification of compound **4** with potassium methacrylate in dry DMF at 65 °C for 4 h and recrystallized from ethanol with 85% yield. ^{1}H NMR, ($CDCl_3$, ppm): 7.865 (d, 4H, aromatic), 6.983 (d, 4H, aromatic), 6.100 (s, 1H, $=CH_2$), 5.543 (s, 1H, $=CH_2$), 4.162 (t, 2H, $COOCH_2$), 4.019 (t, 4H, OCH_2), 3.652 (t, 2H, CH_2OH), 1.946 (s, 3H, CH_3), 1.582–1.846 (m, 8H, aliphatic), 1.458–1.532 (m, 8H, aliphatic). IR (KBr): 3312 (OH), 1703 (–CO–, ester), 1637 ($CH_2{=}CH(CH_3)$) cm^{-1}.

*2.2.6. 6-{4-[4-(2-(α-bromoisobutyryloxy)hexyloxy)phenylazo]phenoxy}hexyl methacrylate (**I**)*

M (0.01 mol) and TEA (1.1 g, 0.011 mol) was dissolved in 30 ml of anhydrous THF in 100 ml of flask which was cooled in ice bath. Then α-bromoisobutyryl bromide (2.53 g, 0.011 mol) dissolved in 5 ml of THF was dropwise added to the mixture. Then the mixture was stirred at room temperature for 24 h. The precipitated was filtered from the reaction mixture, and the filtrated was added into 300 ml of water and then filtered. The solid was recrystallized twice from ethanol and yellow product was gained with 83% yield. ^{1}H NMR ($CDCl_3$, ppm): 7.876 (d, 4H, aromatic), 6.997 (d, 4H, aromatic), 6.104 (s, 1H, $=CH_2$), 5.554 (s, 1H, $=CH_2$), 4.200 (m, 4H, $COOCH_2$), 4. 037 (t, 4H, OCH_2), 1.946 (s, 3H, CH_3), 1.928 (s, 6H, CH_3), 1.840 (m, 4H, aliphatic), 1.730 (m, 4H, aliphatic), 1.507 (m, 8H, aliphatic). IR (KBr): 1734 (–CO–, ester), 1704 (–CO–, ester), 1636 ($CH_2 {=}C(CH_3)$) cm^{-1}.

2.3. Preparation of polymers

Homopolymer and copolymers were synthesized by using Cu(I)Br complexed with HMTETA as the catalyst, and the comonomer-to-catalyst ratio, $\mu = ([I]_0 + [M]_0)/[CuBr]_0$, was fixed at 50. A representative example is as follows (**P2**): CuBr (1.8 mg, 0.013 mmol), **I** (253 mg, 0.40 mmol) and **M** (192 mg, 0.40 mmol) were mixed in a 10 ml ampule bottle, degassed and filled with nitrogen. HMTETA (3.5 μl, 0.013 mmol) in 2 ml of anisole were added through a syringe. The mixture was degassed by three cycles of freeze–pump–thaw procedures and sealed under nitrogen. After 30 min stirring at room temperature, the ampule was placed in the preheated 80 °C oil bath for 40 h. The solution was passed through a neutral Al_2O_3 column with THF as eluent to remove the catalyst. The yellow filtrate was concentrated under reduced pressure and reprecipitated twice in methanol. The yellow polymer was collected by filtration and dried under vacuum. Yield: 231 mg (53%).

3. Results and discussion

3.1. Synthesis

The synthetic route to branched polymers is outlined in Scheme 2. The curved lines represent polymer chains. A*, B*, and M* are active units, whereas a, b, and m are reacted ones. A is a methacryloyl group with azobenzene moiety. For the study of the influence of the degree of branching on the properties of polymers, the homopolymer with azobenzene unit, **P1**, was synthesized by using **I** as inimer. Simultaneously, four copolymers **P2**–**P5** were prepared by using **I** and **M**, respectively, with different comonomer ratio, γ. Detailed experimental conditions and results are given in Table 1. For both of the five polymers, the initial monomer and inimer concentration ($[I]_0 + [M]_0$) and $\mu = ([I]_0 + [M]_0)/[CuBr]_0$ were kept constant ($[I]_0 + [M]_0 = 0.4$ M, $\mu = 50$), whereas the polymerizations time was 40 h in order to control its molecular weights and total conversion. The molar mass characteristics were determined by using GPC. All samples show narrow molecular weight distribution (MWD) in the range of 1.20–1.46. The elution curves shift toward higher molecular weights with increasing comonomer ratio, γ (as shown in Fig. 1). The number- and weight-average molecular weights of the polymers consistently increase with γ (see Table 1), which implied the polymerization could be controlled under the above condition.

As the relation between molecular weight and hydrodynamic volume of branched polymers differ substantially

Table 1
Self-condensing vinyl copolymerization of inimer and monomer at different comonomer ratios γ

Polymer	Monomer	Inimer	γ^a	M_n^{b} (GPC)	M_w/M_n^{c}	DB_{theo}^{d}	Yield (%)
P1		I	0	8600	1.21	0.46	61
P2	M	I	1	8700	1.20	0.49	53
P3	M	I	2	9900	1.24	0.43	58
P4	M	I	10	14,500	1.42	0.17	65
P5	M	I	25	19,600	1.46	0.08	69

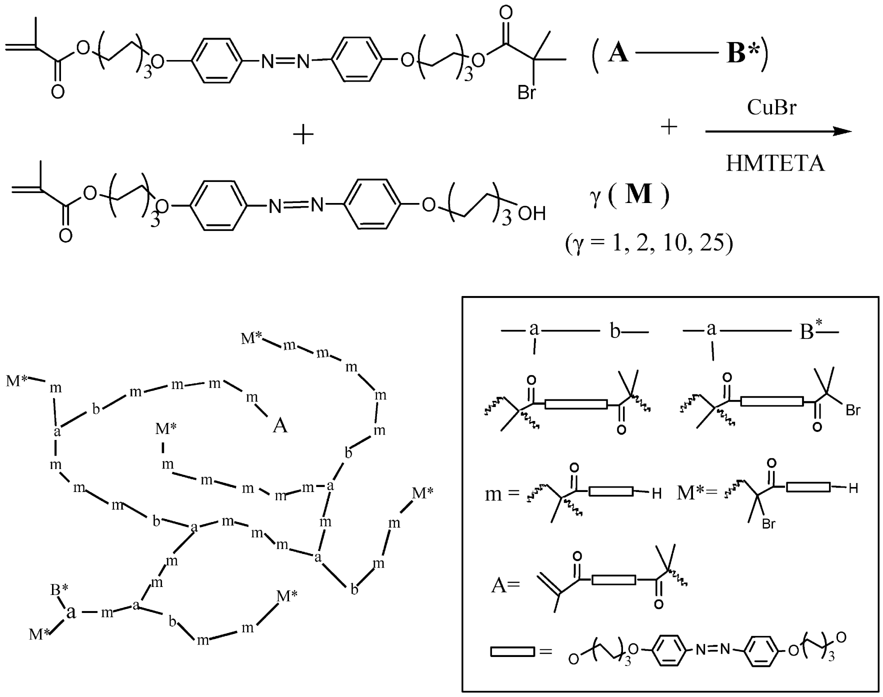
Polymerization at 80 °C with CuBr/HMTETA at a constant comonomer-to-catalyst ratio, $\mu = ([I]_0 + [M]_0)/[CuBr]_0 = 50$.

[a] $\gamma = [M]_0/[I]_0$.

[b] Number-average molecular weight, $M_{n(GPC)}$, determined by GPC.

[c] Polydispersity determined by GPC.

[d] Theoretical degree of branching as determined using Eq. (1) and (2).



Scheme 2. Synthesis and schematic representation of branched polymethacrylates via self-condensing vinyl copolymerization.

from linear ones, the molecular weights established by GPC using universal calibration will depend on the comonomer ratio, γ. According to theory (assuming equal reactivity of active centers [27]), the number-average degree of polymerization, P_n, increases drastically with conversion of the comonomer, X_M, and the polydispersity index, M_w/M_n, decreases with γ. The molecular weight and the molecular weight distribution obtained experimentally were lower than the calculated ones. The observation of finite molecular weight averages can be explained by the occurrence of the cyclization reaction, in which an active center reacts intramolecularly with the double bond, forming a poly-initiator containing one loop. Its presence limits the molecular weights of branched polymers obtained by SCVCP as well as SCVP and narrows the molecular weight distribution [26].

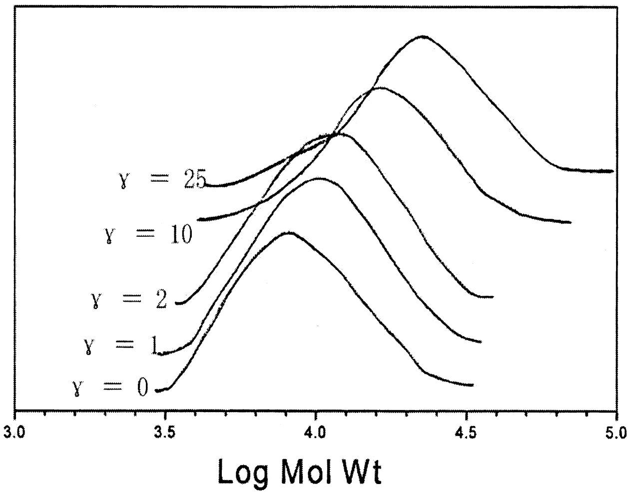


Fig. 1. GPC curves of **P1** to **P5**.

3.2. Degree of branching

Fig. 2 shows the respective ^{1}H NMR spectra of branched **P1** obtained by a homo-SCVP of **I** and **P2**, **P3** obtained by SCVCP. The signals at region 1 belong to the $CDCl_3$ and phenyl rings. Two signals at 6.16 and 5.60 ppm of region 2 arise from the two methylene protons of the remained double bond that could not be polymerized as the first initiator of chain. The peaks of region 3 correspond to the protons of the ethylene linkage. It could be found that a new peak appeared at about 3.82 ppm, which came from the protons of methylene in **M** (as shown in Fig. 2(b) and (c)), and the proportion of peaks at 4.50 ppm diminished gradually from (a) to (c). It was consistent with the increasing of γ. The peaks at about 1.9–2.0 ppm in region 4 are the protons which are ascribed to B^*, M^*, and A. And the peaks at the range of 0.8–1.4 ppm, region 5, are assigned to the protons of methyl of a, b, m and the backbone. About the method of Müller [26], the degree of branching (DB) can be determined by calculating the relative proportion of B^* and b groups in ^{1}H NMR, such as poly(BPEA) [28–32]. But in the case of polymers in this study, the proportion of B^* and b could not be determined by this method because of overlapping signals of methyl protons in the polymer backbone with the methyl protons from the B^* and b groups.

According the theory of SCVCP, the comonomer ratio, γ, can be directly related to the degree of branching [27]. Assuming equal reactivity of all active sites, the degree of

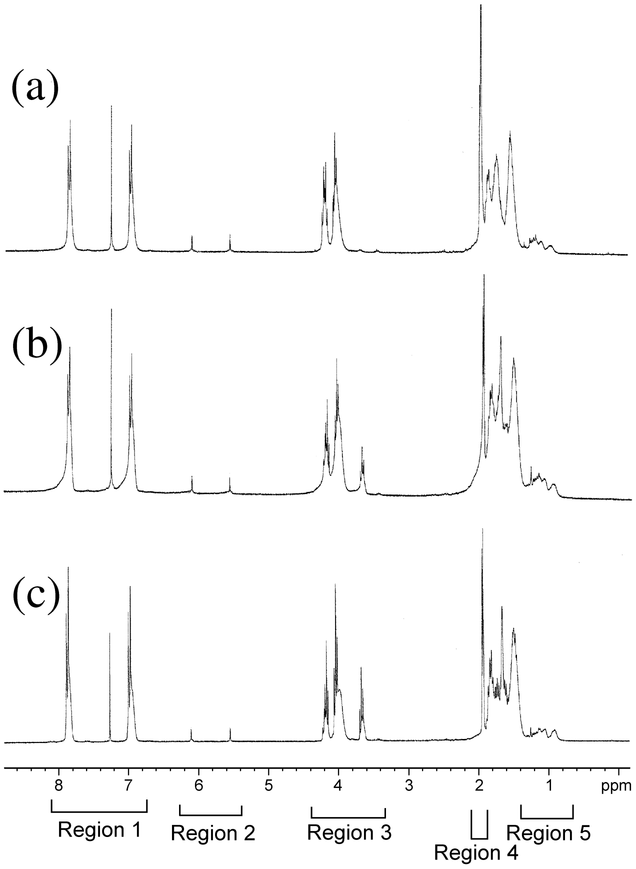


Fig. 2. ^{1}H NMR spectra in $CDCl_3$ of the polymers **P1**, **P2** and **P3** obtained by SCVP of **I** and by copolymerization of **I** and **M**. (a) **P1**. (b) **P2**, and (c) **P3**.

branching obtained from the theory, DB_{theo}, at full conversion can be represented as

$$DB_{theo} = \frac{2(1 - e^{-(\gamma+1)})(\gamma + e^{-(\gamma+1)})}{(\gamma + 1)^2} \tag{1}$$

If the reactivities of the various active centers are not equal, the dependences are more complex and DB may be higher or lower [34]. However, for the limiting case of high comonomer ratios, $\gamma \gg 1$, the relation becomes very simple and does not depend on the reactivity ratios

$$DB_{theo} \approx 2/(\gamma + 1) \tag{2}$$

In the case of $\gamma = 25$, theory predicts $DB_{theo} = 0.077$. We calculated a fraction of branched units $f_B = DB_{theo}/2 = 0.038$, i.e. which corresponds to 38 branching points in 1000 monomer units or an average of 25 monomer units between branch points. In this copolymerization system, **I** used as an AB* inimer contains the methacrylate and bromoisobutylate groups, both of which form tertiary radicals, and **M** used as a comonomer also generates a tertiary radical. The tertiary α-bromoester dormant species formed during the reaction should have a reactivity similar to the 2-bromoisobutylate found on the AB* inimer. Hence, the difference in the rate constants for the six possible propagation reactions of the different centers is considered to be small. However, a slow deactivation of the propagating radical was shown to lead faster apparent reactivity ratios. When the reactivities of the various active centers are not equal, the dependences are more complex, and the degree of branching may be higher or lower, depending upon the systems.

With ATRP, nearly every chain in homopolymer should contain a halogen atom at its end group, if termination and transfer are essentially absent. This halogen atom can be replaced through a variety of reactions leading to end-functional polymers and used as the initiating part for polymerization of a second monomer. Halogen atom displacement reactions from hyperbranched polystyrene and polyacrylated have also been reported [33,34]. Hyperbranched polymers can further initiate polymerizations forming hyperstar (dendrigraft) polymers [35]. In the case of ideal SCVCP via ATRP, the resulting branched polymers carry one bromoester function per inimer unit, and the functionality decreased with comonomer composition. The bromine contents of the branched polymers are dependent upon the comonomer composition in the feed [28], but it is hard to determine the dependence of bromine content on γ in this paper because of signals of methyl protons are overlapping. Furthermore, the hydroxyl in **P2**–**P5** can reacted with other functional groups to introduce more interesting properties.

3.3. UV–vis spectroscopy

The UV–vis spectra of azobenzene chromophore were observed for solutions and films of homopolymer **P1** and all copolymers. As an example, Fig. 3 compares the UV–vis spectra of **P2** in the solution and **P1**, **P3**, and **P5** in the solid state, before and after UV exposure at 365 nm, reaching the photostationary state. The five polymers showed the nearly same spectra of azobenzene chromophore in the THF solution. They all exhibited one strong absorption band and one weak band which were related to $\pi-\pi^*$ and n-π^* transition bands of the *trans* and *cis* azobenzene, respectively (as shown in Fig. 3(A)). Under UV irradiation at 365 nm, the five branched polymers all showed a typical spectral variation of azobenzene chromospheres resulted from the *trans*-to-*cis* photoisomerization. The change of the UV–vis absorption spectra of the **P2** in THF solution was shown in Fig. 3(A). It can be seen that the intensity of $\pi-\pi^*$ transition band at about 358 nm decreased while that of n-π^* transition band at 444 nm increased gradually. The photostationary state was obtained after irradiation for 25 s. Keeping in dark, the contents of *trans* azobenzene of all polymers were recovered completely.

The as-cast films of homopolymer **P1** and copolymer **P2**–**P5** were cast from 1 wt% solution in THF onto quartz glass and dried at 50 °C under vacuum to remove the solvent. The spectra of **P1**, **P3** and **P5** were shown in Fig. 3(B)–(D). It is interesting to see that the *trans*–*cis* isomerization of the three films were evidently different.

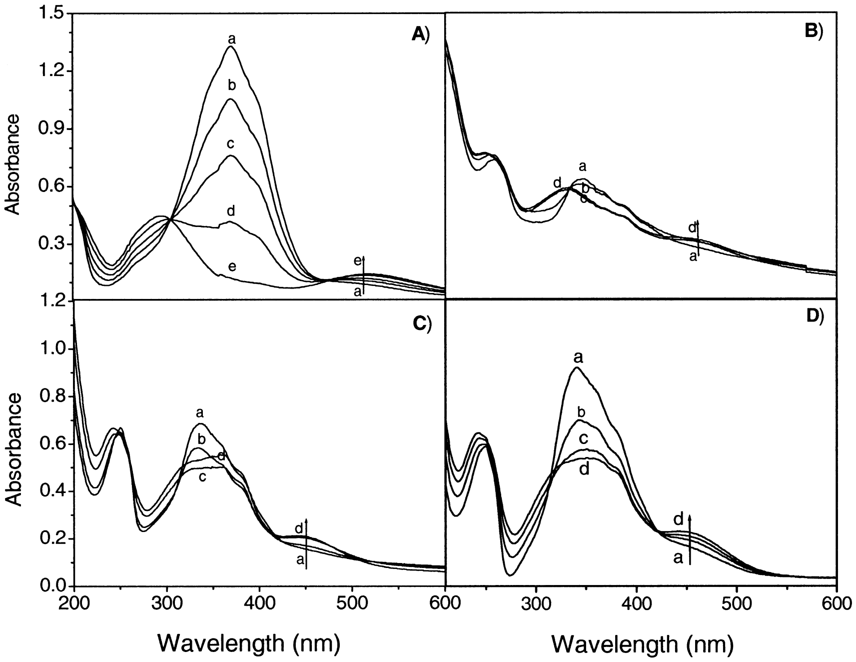


Fig. 3. (A) Spectral changes of **P2** in THF solution during UV irradiation. The irradiation time is (a) 0 s, (b) 5 s, (c) 10 s, (d) 15 s, (e) 25 s, respectively. (B, C, and D) The spectral changes of **P1**, **P3**, and **P5** on the quartz glass under UV irradiation. The irradiation time is (a) 0 s, (b) 60 s, (c) 2 min, (d) 4 min.

The film of **P1** (as shown in Fig. 3(B)) showed a complicated photochemical procedure with the irradiation of 365 nm light. In the early stage of the irradiation for 1 min, the absorbance at 338 nm decreased successively, indicating simple *trans–cis* isomerization. And it can be proved by the increase of absorbance of 440 nm. When prolonged the irradiation time, the intensity of the absorbance of *trans*-isomer continually decreased, but the maximum absorbance continued to blue-shift to 321 nm. It suggested that the appearance of H-aggregation of *trans*-isomer of azobenzene chromophore with the irradiation of 365 nm light. The *trans–cis* isomerization of **P2** was like **P1** (the spectra were not shown).

The initial spectra of film of **P3** were like **P2**, the maximum absorbance of *trans*-isomer was located at 337 nm, which was blue-shift compared with the spectra in the solution (as shown in Fig. 3(C)). When it was irradiation with 365 nm light, the absorbance at 440 nm also increased. However, with further irradiation (2–4 min), the absorbance increased smoothly, and the spectra became much broader. (The shoulder at 360 nm was assigned to the isolated monomeric absorption.) These processes might be related with the reorganization of the azobenzene chromophores during the *trans–cis* isomerization due to insufficient free volume caused by the strong H-aggregation and perpendicular alignment of the chromophores [36].

When irradiated the film of the **P5**, the same phenomena was found like the normal linear azo-containing polymer (as shown in Fig. 3(D)) [17,18]. The maximum absorbance of *trans*-isomer on the film was blue-shifted compared with the spectra in the solution. The spectra decreased and the maximum absorbance red-shifted with extends of the irradiation time. The different spectra change of **P1–P5** on the film under irradiation of 365 nm light showed that the branched structure of polymers have strong influence on the *trans–cis* isomerization [17,18]. We hope that the special photoisomerization in the films of the hyperbranched azopolymers may find some contributions to photosensitive films concerning photo-induced holographic gratings, optical films, LC alignment layers and other optical switch devices.

4. Conclusions

We have synthesized a series of hyperbranched homopolymer and copolymers with functional azobenzene units in the side chain by using the newly developed SVCP and copolymerization (SCVCP) methods. These gained polymers were characterized by GPC and ^{1}H NMR measurements and found they had narrow polydispersity index in the range of 1.20–1.46. In addition, the molecular weights, the composition and the degree of branching structure of the polymers can be adjusted by an appropriate choice of the comonomer composition, γ. The UV–vis spectra in the solutions showed the five polymers can take place typical *trans–cis–trans* photoisomerization reaction under UV irradiation. On the films, the *trans–cis* isomerization of the azobenzene chromophore in the different degree of branching polymers was markedly different. The branched structure of the polymers had an important influence on the optical properties. In summary, it is possible to design various hyperbranched azo-polymers by smartly exploiting the architecture in the polymer and could find some possible application in the photosensitive devices.

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