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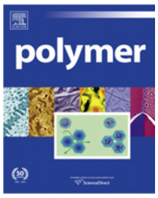

Synthesis and characterization of azobenzene-functionalized poly(styrene)-*b*-poly(vinyl acetate) via the combination of RAFT and "click" chemistry

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Here, we described a strategy for preparing well-defined block copolymers, poly(styrene)-*b*-poly(vinyl acetate) (PS-*b*-PVAc), containing middle azobenzene moiety via the combination of the reversible addition-fragmentation chain transfer (RAFT) polymerization and "click" chemistry. Firstly, a novel RAFT agent containing α-alkyne and azobenzene chromophore in R group, 2-(3-ethynylphenylazophenoxy carbonyl)prop-2-yl-9H-carbazole-9-carbodithioate (EACDT), was synthesized and used to mediate the RAFT polymerization of styrene (St). Well-defined α-alkyne end-functionalized poly(styrene) (PS) was obtained. Secondly, the RAFT polymerization of vinyl acetate (VAc) was conducted using functionalized RAFT reagent with ω-azide structure in Z group, *O*-(2-azidoethyl) *S*-benzyl dithiocarbonate (AEBDC). Well-defined ω-azide end-functionalized poly(vinyl acetate) (PVAc) was obtained. Afterwards, the resulting α-alkyne terminated PS was coupled by "click" chemistry with the azide terminated PVAc. The block copolymer, PS-*b*-PVAc, was obtained with tailored structures. The products from each step were characterized and confirmed by GPC, ^{1}H NMR, IR and differential scanning calorimetry (DSC) examination. Kinetics of the *trans-cis-trans* isomerization from azobenzene chromophore in PS-*b*-PVAc and PS were investigated in $CHCl_3$ solutions.

1. Introduction

The "living"/controlled free radical polymerization (LFRP) techniques have been fast developed in the past decades. Many efficient systems have been well developed especially for the atom transfer radical polymerization (ATRP) [1], reversible addition-fragmentation chain transfer (RAFT) polymerization [2] and nitroxyl radical mediated polymerization (NMP) [3]. The development of LFRP makes it convenient to realize precise controlling over the polymerization process (controlled molecular weights and low polydispersity index) under mild conditions. Many complex structure polymers covered with a wide monomers range have been synthesized via LFRP, such as block, star, and other complex architectures for styrene (St), (meth)acrylate and so on. However, it is still a challenge to control free radical homo- and copolymerization of vinyl acetate (VAc), a typical unconjugated vinyl monomer, due to the high reactivity of its propagation radicals, which undergo radical–radical termination and chain transfer on the polymer and monomer [4]. There are limited LFRP techniques to control the free radical polymerization of VAc: RAFT polymerization using xanthates [5] or dithiocarbamates as RAFT agents [6], NMP of VAc using the system of *i*-Bu_3Al/2,2′-bipyridine/TEMPO [7], iodides [8], cobalt-mediated [9], iron-catalyzed [10] radical polymerization, and photo-living radical polymerization [11].

Till very recently reported by Rizarrdo et al. it was able to prepare block copolymer of VAc with conjugated vinyl monomer, such as styrene and (meth)acrylate, using a new class of "switchable" RAFT agents [12]. On the other hand, there were several routes reported for the synthesis of well-controlled PS-*b*-PVAc block copolymers by combination of different methods. For example, Zi-Chen Li et al. obtained well-defined block copolymer PS-*b*-PVAc by combination of ATRP and RAFT polymerization [13]. Combination of cobalt-mediated radical polymerization (CMRP) and ATRP had also been performed to be a novel method [14].

Recently, Sharpless et al. successfully optimized 1,3-dipolar cycloaddition of azide and terminal alkyne leading to 1, 2, 3-triazole via copper (I) catalysis [15]. This concept of popular "click" chemistry gained most attention for its high efficiency, quantitative yields and selectivity under mild reaction conditions [16]. This novel method had been successfully applied to block copolymer PS-*b*-PVAc synthesis. Stenzel and his coworkers synthesized two RAFT agents with azide or alkyne group [17]. They used these RAFT agents to prepare homopolymers of poly(vinyl acetate) and poly(styrene) with terminal azide and alkyne group respectively. Then well-defined block copolymer, PS-*b*-PVAc was prepared via "click" chemistry between these two homopolymers.

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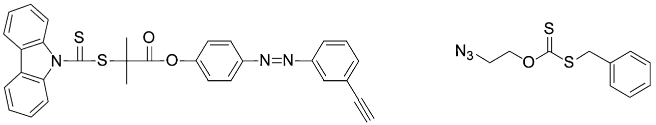
Azobenzene-based materials have gained a great deal of attention due to potential application in fascinating photo-responsive variations [18,19], such as optical data storage, liquid crystal displays, optical switching, holographic surface relief gratings (SRGs) and so on. Meanwhile, azobenzene-terminated polymers have also been applied in photochromic probes [20] and photo-responsive polymers [21]. Lydie Viau et al. reported azobenzene-based ATRP initiator to synthesize photoisomerizable star-shaped polymer by atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) [22]. Photoisomerization properties of such new metallochromophores have been studied. Our group also prepared well-defined azobenzene-terminated poly(methyl methacrylate) (PMMA) [23] via ATRP and poly(styrene) (PS) [24] via RAFT polymerization, respectively. These polymers showed typical *trans-cis* isomerization behavior under UV light irradiation.

Herein, we synthesized a novel α-alkyne RAFT reagent containing azobenzene chromophore, 2-(3-ethynylphenylazophenoxy carbonyl)prop-2-yl-9H-carbazole-9-carbodithioate (EACDT) and a functionalized xanthate agent with ω-azido-Z group, *O*-(2-azidoethyl) *S*-benzyl dithiocarbonate (AEBDC) [25], as shown in Scheme 1. Subsequently, the RAFT polymerization of styrene and VAc was carried out using EACDT and AEBDC as RAFT reagent, respectively. Afterwards, the resulting α-alkyne terminated poly(styrene) (PS) was coupled by "click" chemistry with the ω-azido-terminated poly(vinyl acetate) (PVAc) to obtain well-defined block copolymer poly(styrene)-*b*-poly(vinyl acetate) containing middle azobenzene moiety. The *trans-cis-trans* isomerization of PS-*b*-PVAc and PS with azobenzene chromophore was investigated in $CHCl_3$ solution. It showed adjustable isomerization rate before and after "click" reaction. The current work opened the opportunity for synthesizing conjugated and unconjugated vinyl block copolymers with azobenzene structure incorporated.

2. Experimental section

2.1. Materials

3-Ethynylaniline (≥98%; Aldrich), phenol (analytical reagent; Shanghai Chemical Reagent Co. Ltd, Shanghai, China), carbazole (98%; Aldrich), carbon disulfide (analytical reagent; Shanghai Chemical Reagent Co. Ltd, Shanghai, China), 2-bromoisobutyryl bromide (98%; Aldrich), and sodium azide (≥99.5%; Aldrich) were used as received. Vinyl acetate (99%; Shanghai Chemical Reagents Co.) was purified by passing over a column of basic alumina and subsequently distilled under reduced pressure and kept in a refrigerator at −15 °C. Styrene (analytical reagent; Shanghai Chemical Reagent Co. Ltd, Shanghai, China) was washed with an aqueous solution of sodium hydroxide (5 wt%) three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, the monomers were distilled twice under reduced pressure, and kept below −15 °C. 2,2′-Azobisisobutyronitrile (AIBN, 99%; Shanghai Chemical Reagent Co. Ltd, China) was recrystallized three times from ethanol and dried in vacuum at room temperature. Other reagents were purified using standard procedure before use.



EACDT **AEBDC**

Scheme 1. Chemical structures of 2-(3-ethynylphenylazophenoxycarbonyl)prop-2-yl-9H-carbazole-9-carbodithioate (EACDT) and *O*-(2-azido-ethyl) *S*-benzyl dithiocarbonate (AEBDC).

2.2. Synthesis of 2-(3-ethynylphenylazophenoxy-carbonyl)prop-2-yl-9H-carbazole-9-carbodithioate (EACDT)

The α-alkyne RAFT reagent EACDT containing azobenzene chromophore was synthesized according to the route showed in Scheme 2.

2.2.1. 3′-Ethynylphenyl-(4-hydroxy)azobenzene (1)

3-Ethynylaniline (5.85 g, 50 mmol) was added dropwise to a solution of concentrated HCl (37%, 15 mL) in deionized water (30 mL). The mixture was stirred in an ice bath to keep the reaction temperature at 0–5 °C. Then a water solution (10 mL) of sodium nitrite (3.50 g, 50.7 mmol) was added within 10 min. The mixture was stirred at 0–5 °C for further 60 min. A yellow transparent diazonium salt solution was obtained. A coupling solution was prepared as follows: phenol (8 g, 85 mmol), NaOH (4 g, 100 mmol) and $NaHCO_3$ (4.2 g, 50 mmol) was dissolved in 250 mL of water under vigorous stirring at 0–5 °C. Then the diazonium salt solution was added dropwise to the coupling solution with the temperature of 0–5 °C. The final mixture was stirred at 5 °C for 3 h. The precipitate was collected by filtration, washed with deionized water three times, and dried under vacuum. The crude product was purified by recrystallization from ethanol. Compound **1** was obtained as red-orange crystal (10.0 g, yield: 90.0%).

The characteristic analytical data involved are as follows: ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.04–7.97 (s, 1H, ArH), 7.94–7.83 (m, 3H, ArH), 7.62–7.52 (d, 1H, ArH), 7.50–7.42 (m, 1H, ArH), 7.00–6.91 (d, 2H, ArH), 5.36–5.27 (s, 1H, ArOH), 3.17–3.10 (s, 1H, $ArC{\equiv}CH$); Elemental analysis: calculated (%): C 75.66, H 4.54, N 12.60; found (%): C 75.31, H 4.34, N 13.11.

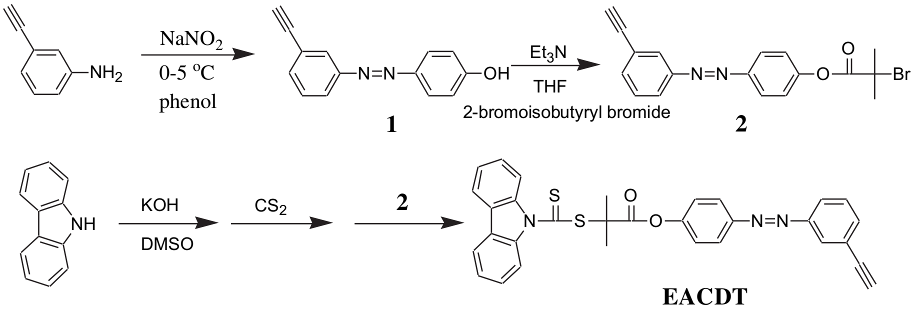
2.2.2. 2-Bromo-2-methylpropionic acid 4-(3-ethynyl-phenylazo) phenyl ester (**2**)

The compound **1** (6.66 g, 30 mmol), dry THF (150 mL) and dry triethylamine (6.06 g, 60 mmol) was added to a 250 mL three-necked flask. The solution was stirred in an ice bath. A solution of 2-bromoisobutyryl bromide (10.35 g, 45 mmol) in dry THF (30 mL) was added dropwise to the mixture with the temperature at 0–5 °C. The reaction mixture was vigorously stirred for another 3 h at 0–5 °C, and then at room temperature overnight. After filtration, the filtrate was evaporated under vacuum. The remaining yellow mixture was dissolved in dichloromethane and washed with 5% Na_2CO_3 aqueous solution followed with deionized water for three times. The organic solution was dried with anhydrous $MgSO_4$ overnight. Then, dichloromethane solvent was evaporated under a reduced pressure. The final crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5) to yield compound **2** as saffron solid (6.32 g, 62.1%).

The characteristic analytical data involved are as follows: ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.07–8.03 (s, 1H, ArH), 8.02–7.97 (d, 2H, ArH), 7.93–7.88 (d, 1H, ArH), 7.63–7.57 (d, 1H, ArH), 7.52–7.44 (m, 1H, ArH), 7.35–7.28 (d, 2H, ArH), 3.17–3.13 (s, 1H, $ArC{\equiv}CH$), 2.12–2.08 (s, 6H, $-CH_3$); Elemental analysis: calculated (%): C 58.04, H 4.07, N 7.55; found (%): C 57.82, H 4.33, N 7.83.

2.2.3. 2-(3-Ethynylphenylazophenoxycarbonyl)prop-2-yl-9H-carbazole-9-carbodithioate (EACDT)

RAFT agent EACDT was synthesized according to the following procedure: carbazole (1.67 g, 10 mmol) was added to a suspension of KOH (0.56 g, 10 mmol) in DMSO (25 mL) under vigorous stirring. The reaction mixture was stirred overnight at room temperature.



Scheme 2. Synthetic route of 2-(3-ethynylphenylazophenoxycarbonyl)prop-2-yl-9H-carbazole-9-carbodithioate (EACDT).

Carbon disulfide (0.76 g, 10 mmol) was added dropwise into this mixture, and the resultant reddish solution was stirred for 10 h at room temperature, followed by adding slowly compound **2** (3.71 g, 10 mmol) in DMSO (20 mL). The final mixture was stirred for 12 h at room temperature. The resultant reaction mixture was poured into large amount of deionized water, and orange red solid was obtained by filtration. The crude product was purified by recrystallization three times from ethanol. The pure EACDT was obtained as yellow crystal (yield: 2.72 g, 51%).

The characteristic analytical data involved are as follows: ^{1}H NMR ($CDCl_3$, δ): 8.42–8.48 (d, 2H, carbazole–H), 7.95–8.06 (m, 5H, carbazole–H and Ar–H), 7.83–7.94 (d, 1H, Ar–H), 7.57–7.62 (d, 1H, ArH), 7.43–7.52 (m, 3H, carbazole–H and Ar–H), 7.33–7.41 (m, 4H, carbazole–H and Ar–H), 3.13–3.17 (s, 1H, ArC≡CH), 2.02–2.10 (s, 6H, $-CH_3$). UV–vis: $\lambda_{max} = 315$ nm (CH_3Cl). Elemental analysis: calculated (%): C 69.77, H 4.34, N 7.87, S 12.02; found (%): C 69.79, H 4.50, N 7.91, S 12.35. The ^{1}H NMR spectrum of EACDT is shown in Fig. 1.

2.3. *Synthesis of O-(2-azidoethyl) S-benzyl dithiocarbonate (AEBDC)*

AEBDC was synthesized as described in a previous report [25]. The characteristic analytical data involved are as follows: ^{1}H NMR ($CDCl_3$, δ): 7.25–7.40 (m, 5H, Ar–H), 4.76 (t, 2H, CH_2–O–), 4.42 (s, 2H, CH_2–S–), 3.65 (t, 2H, CH_2–N_3). Elemental analysis: calculated (%): C 47.41, H 4.38, N 16.59; found: C 47.24, H 4.55, N 16.45.

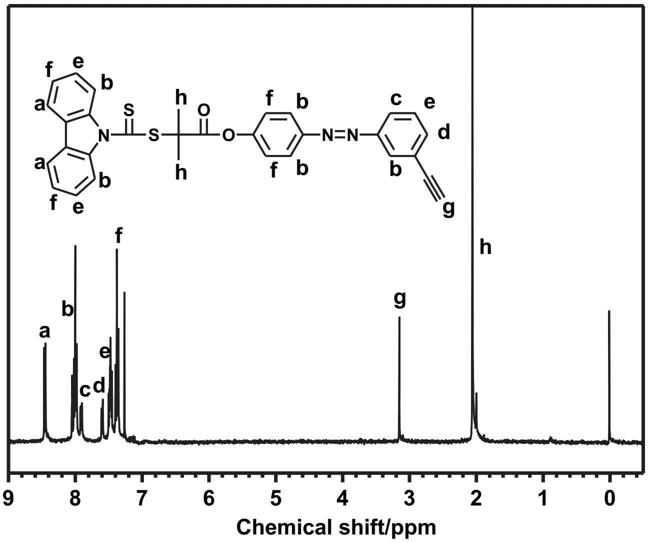


Fig. 1. ^{1}H NMR spectrum of the RAFT agent EACDT in $CDCl_3$.

2.4. *RAFT polymerization of styrene using EACDT as RAFT agent*

The procedure of RAFT polymerization of styrene (St) was as follows: A dry 5 mL ampoule tube was filled with St (3 mL, 26.1 mmol), EACDT (0.0463 g, 0.087 mmol) ($[St]_0$: $[EACDT]_0 = 300$: 1) and anisole (2 mL). The content was purged with argon for 10 min to eliminate the oxygen. Then the ampoule was flame-sealed. The polymerization reaction was performed in an oil bath by a thermostat at 115 °C and terminated after 12 h. The contents were diluted with 10 mL tetrahydrofuran (THF) and precipitated into 250 mL methanol. The precipitate was filtrated and dried to a constant weight at room temperature in vacuum. The conversion of polymer was determined by gravimetry.

2.5. *RAFT polymerization of vinyl acetate (VAc) using AEBDC as RAFT agent*

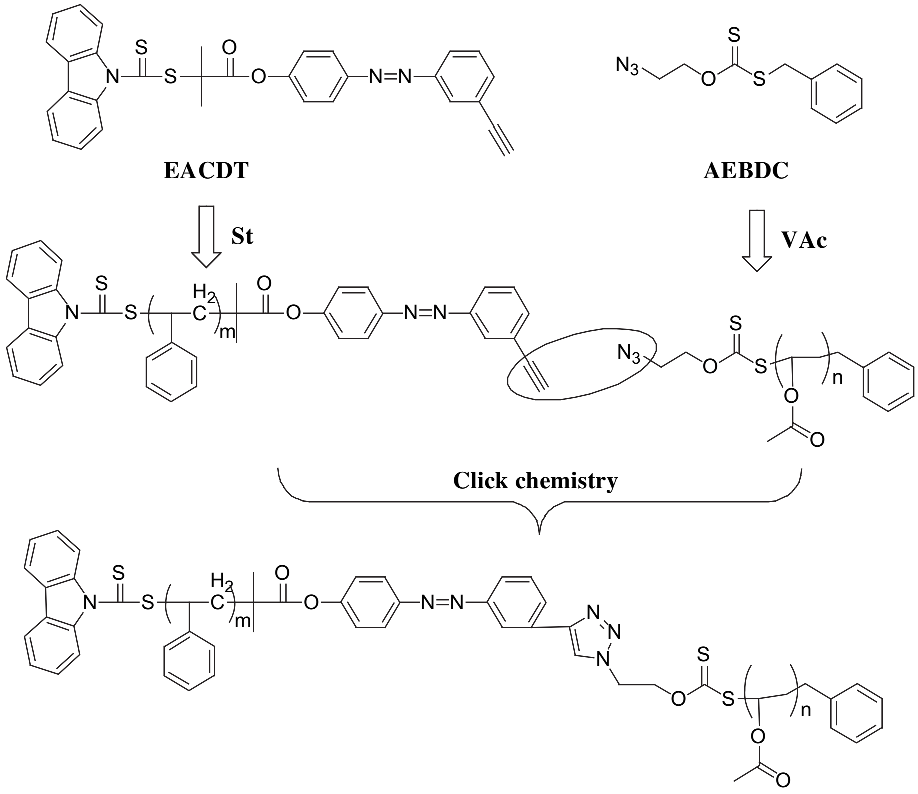
The ω-azido-terminated poly(vinyl acetate) (PVAc) was synthesized as described in a previous report [25]. A dry 10 mL ampoule tube was filled with 10 mL (118 mmol) of VAc, 0.448 mg (1.77 mmol) of AEBDC and 48.4.6 mg (0.295 mmol) of AIBN with a predetermined molar ratio ($[VAc]_0$: $[AEBDC]_0$: $[AIBN]_0 = 200$: 3: 0.5). The content was purged with argon for 20 min to eliminate the oxygen. Then the ampoule was flame-sealed and placed in an oil bath held by a thermostat at 80 °C to polymerize. After a preset reaction time, the polymerization was terminated. The reaction mixture was diluted with 10 mL THF and precipitated in 250 mL of hexane. The polymer was obtained by filtration and dried at room temperature in vacuum to a constant weight. The conversion of polymerization was determined gravimetrically.

2.6. *"Click" reactions of the α-alkyne-terminated poly(styrene) (PS) with the ω-azido-terminated poly(vinyl acetate) (PVAc)*

The synthetic route was shown in Scheme 3. A dry 10 mL ampoule tube was filled with a solution of PS (0.1 mmol), PMDETA (0.5 equiv), and PVAc (1 equiv) in THF (10 mL). The content was purged with argon for 10 min to remove oxygen. Then CuBr (0.5 equiv) was added under argon atmosphere. The content was purged with argon for another 10 min. After that, the ampule was flame-sealed. "Click" reaction was performed at 80 °C for 24 h. The reaction mixture was passed through a column of neutral alumina. The polymer was obtained by precipitating reaction mixture into 250 mL petroleum ether followed by filtration and vacuum drying.

2.7. *Analysis and characterizations*

The number-average molecular weights (M_ns) and molecular weight distributions (M_w/M_ns) of the polymers were determined with a Waters 1515 gel permeation chromatographer (GPC)



Scheme 3. Synthetic route of block copolymers poly(styrene)-*b*-poly(vinyl acetate) containing azobenzene moiety.

equipped with a refractive index detector, using HR1, HR3, and HR4 column with a molecular weight range of 100–500,000 calibrated with PS and PMMA standard samples. THF was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30 °C. ^1H NMR spectra were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument, using $CDCl_3$ as solvent, tetramethylsilane (TMS) as the internal standard. Elemental analysis of C, H, N and S were conducted with an EA1110 CHNO-S instrument. The UV–vis spectra were determined on a Hitachi U-3900 spectrophotometer at room temperature. Differential scanning calorimetry (DSC) was performed using a TA instruments DSC2010 with a heating/cooling rate of 10 °C min^{-1} under a continuous nitrogen flow. FT-IR spectra were recorded on a Nicolette-6700 FT-IR spectrometer.

3. Results and discussions

3.1. RAFT polymerization of styrene (St) and vinyl acetate (VAc)

According to reference [26], dithiocarbamates can be used as efficient RAFT agents to control the free radical polymerization of conjugated vinyl monomers due to significantly enhancement of the activity by introducing electron-withdrawing groups on nitrogen atom or the delocalization of the nitrogen electron pair. Moreover, the structure of the N-group within dithiocarbamate has significant effects on the activity of thiocarbonylthio compounds for the RAFT polymerization of St. Our group reported that dithiocarbamate derived from carbazole group in N-group was effective RAFT agent for the RAFT polymerization of St [24,27]. The polymerizations showed good living characteristics. Thus, a novel α-alkyne RAFT agent containing azobenzene chromophore, 2-(3-ethynylphenylazophenoxycarbonyl)prop-2-yl-9H-carbazole-9-carbodithioate (EACDT), was synthesized and used to mediate the RAFT polymerization of styrene (St) for preparing well-defined end-functionalized polymers (PS). The RAFT polymerization of St was carried out in anisole using EACDT as RAFT agent and thermal initiation at 115 °C with molar ratio of $[St]_0$: $[EACDT]_0$ = 300: 1. Detailed experimental conditions and results were listed in Table 1. In order to increase the degree of end-functionality, the monomer conversion was controlled to less than 50%. After the polymerization period of 12 h and 15 h, two poly(styrene) (PS), e.g. PS1 and PS2 were obtained with monomer conversions of 11.7%, and 16.5%. Narrow molecular weight distributions (M_w/M_ns ≤ 1.15) and good agreement between the number-average molecular weights measured by GPC ($M_{n(GPC)}$) and theoretical values ($M_{n(th)}$) indicated that the EACDT was an effective RAFT agent for St polymerization. The theoretical values $M_{n(th)}$ were calculated via Equation (1):

$$M_{n(th)} = [St]_0/[EACDT]_0 \times M_{st} \times \mathrm{Conversion} + M_{EACDT} \qquad (1)$$

Table 1
Characteristics of the end-functionalized homopolymers PS, PVAc and block copolymers PS1-*b*-PVAc, PS2-*b*-PVAc.

Sample	T (°C)	Time (h)	Con./Yield(%)	$M_{n(GPC)}$[f]	$M_{n(th)}$[g]	M_w/M_n
PS1[a]	115	12	11.7[d]	3800	3600	1.10
PS2[a]	115	15	16.5[d]	5000	5100	1.12
PVAc[b]	80	12	27.9[d]	1800	1600	1.19
PS1-*b*-PVAc[c]	80	24	95.2[e]	5100	–	1.34
PS2-*b*-PVAc[c]	80	24	94.7[e]	6700	–	1.21

[a] $[St]_0$: $[EACDT]_0$ = 300: 1, at 115 °C in anisole with thermal initiation. St/anisole = 3:2 (v/v).

[b] $[VAc]_0$: $[AEBDC]_0$: $[AIBN]_0$ = 200: 3: 0.5, at 80 °C in bulk.

[c] Polymers obtained via "click" chemistry using CuBr and PMDETA as catalyst system at 80 °C for 24 h.

[d] Conversion determined by gravimetry.

[e] Yield determined by gravimetry.

[f] $M_{n(GPC)}$: Molecular weight determined by GPC.

[g] $M_{n(th)}$: Theoretical molecular weight calculated via Equation (1).

where, $[\mathrm{St}]_0$ and $[\mathrm{EACDT}]_0$ were the initial concentration of St and EACDT, respectively, M_{St} and M_{EACDT} were the molecular weights of St and EACDT.

VAc can be polymerized under controlled manner via RAFT or MADIX polymerization using xanthates as chain transfer agents. Our group successfully synthesized ω-azido-functionalized xanthate, *O*-(2-azidoethyl) *S*-benzyl dithiocarbonate (AEBDC) [25], and used as chain transfer agent in the polymerization of VAc. The polymerization results showed that AEBDC was an effective chain transfer agent for controlling the polymerization of VAc. Thus, well-controlled poly(vinyl acetate) (PVAc) was obtained with molecular weight of 1800 g/mol and molecular weight distributions of 1.19.

3.2. "Click" chemistry between PS and PVAc

The obtained ω-azido-functionalized PVAc was subsequently involved in "click" chemistry with α-alkyne terminated PS to prepare block copolymers, poly(styrene)-*b*-poly(vinyl acetate) (PS-*b*-PVAc), containing middle azobenzene chromophore. According to reference [28], the copper (I) with PMDETA as ligand was efficient catalyst system for the 1,3-dipolar cycloaddition of organic azides with terminal alkynes. Herein, "click" chemistry of PS and PVAc was conducted using CuBr and PMDETA as catalyst system, THF as solvent at 80 °C. Detailed experimental conditions and results were given in Table 1. PS with molecular weight of 3800 g/mol and 5000 g/mol was combined with PVAc with molecular weight of 1800 g/mol. The obtained block copolymers showed corresponding molecular weight of 5100 g/mol and 6700 g/mol, which were close to the sum value of its original polymers. GPC curves of the homopolymers and block copolymers were shown in Fig. 2. There was an obvious peak shift from the homopolymers to the copolymer product after the "click" coupling. The molecular weight increased from 3800 g/mol to 5100 g/mol. However, the molecular weight distributions of the polymers showed a slight increase, e.g. from 1.12 of PS and 1.19 of PVAc to 1.21 of block copolymer. The reason was due to the presence of small portion of remaining homopolymers. These homopolymers may derive from the nonend-functionalized polymers, PS and PVAc, in the systems. Furthermore, it was difficult to operate at the perfect stoichiometry 1: 1 with homopolymers [17,29], which should be resulted in the remaining of homopolymer after couple reaction.

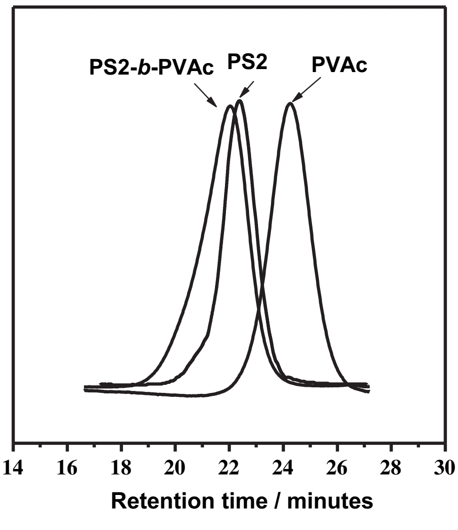


Fig. 2. The GPC curves of the homopolymers PS2 ($M_{\mathrm{n(GPC)}}$ = 5000 g/mol, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.12), PVAc ($M_{\mathrm{n(GPC)}}$ = 1800 g/mol, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.19) and copolymer PS2-*b*-PVAc ($M_{\mathrm{n(GPC)}}$ = 6700 g/mol, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.21).

3.3. End group analysis and thermal characterization

To further confirm the molecular structures, all the polymers were characterized via ^{1}H NMR and FT-IR spectroscopy. Fig. 3 showed the ^{1}H NMR spectroscopy of the homopolymers PS2, PVAc and block copolymer PS2-*b*-PVAc. In the spectrum of PS2, the characteristic signals corresponding to the protons of the alkyne group (a) were observed at around 3.02–3.16 ppm, which indicated that the alkyne group did not participate in RAFT polymerizations. The chemical shifts at around 7.70–8.30 ppm were due to phenyl protons of the azobenzene group (b) and carbazole (b). These results indicated that the moiety of the RAFT agent was attached to the end of PS2. Furthermore, the molecular weight ($M_{\mathrm{n(NMR)}}$ = 5300 g/mol), calculated from the ^{1}H NMR spectrum (Equation (2)) was close to the value obtained by GPC ($M_{\mathrm{n(GPC)}}$ = 5000 g/mol). From these data, it can also be estimated the degree of end-functionality by $M_{\mathrm{n(GPC)}}/M_{\mathrm{n(NMR)}}$. The result indicated that 86% (5000/5800) chains of the polymers were end-functionalized with the azobenzene and alkyne group. The $M_{\mathrm{n(NMR)}}$ was given by Equation (2):

$$M_{n,\mathrm{NMR}} = \left(\frac{I_{1.06-2.30}-6}{3}\middle/\frac{I_{7.69-8.33}}{8}\right)\times M_{\mathrm{St}} + M_{\mathrm{EACDT}} \qquad (2)$$

$I_{1.06-2.30}$ is the integral of the signals (d) at 1.06–2.30 ppm, and $I_{7.69-8.33}$ is the integral of the signals (a) at 7.69–8.33 ppm in Fig. 3 (PS2).

The spectrum of PVAc in Fig. 3 also confirmed that the RAFT agent was successfully attached to the end of polymer chain. Similarly, the molecular weight of PVAc can be calculated from the ^{1}H NMR spectrum ($M_{\mathrm{n(NMR)}}$ = 1900 g/mol). Thus, the degree of end-functionality ($M_{\mathrm{n(GPC)}}/M_{\mathrm{n(NMR)}}$) was 95% (1800/1900). These results were similar to our previous report [25].

Afterwards, the resulting α-alkyne terminated PS2 was coupled via "click" chemistry with the ω-azido-terminated PVAc. The

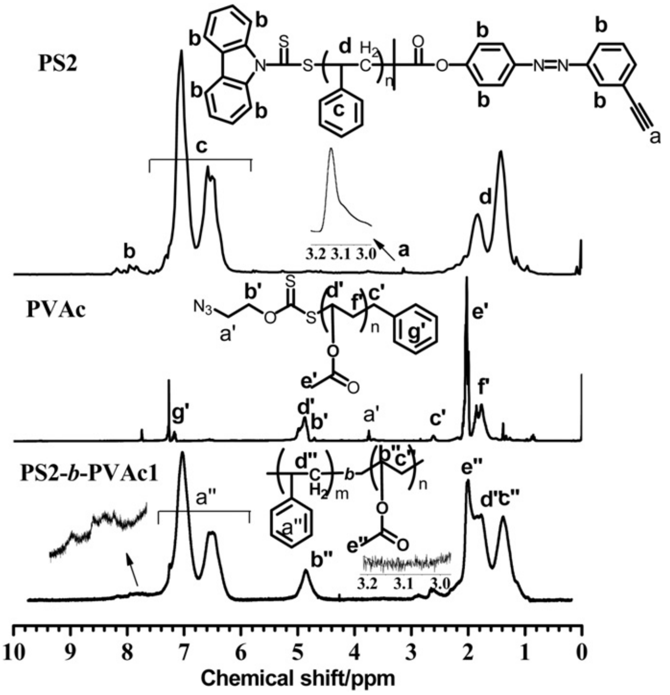


Fig. 3. ^{1}H NMR spectra of the homopolymers PS2 ($M_{\mathrm{n(GPC)}}$ = 5000 g/mol, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.12), PVAc ($M_{\mathrm{n(GPC)}}$ = 1800 g/mol, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.19) and copolymer PS2-*b*-PVAc ($M_{\mathrm{n(GPC)}}$ = 6700 g/mol, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.21).

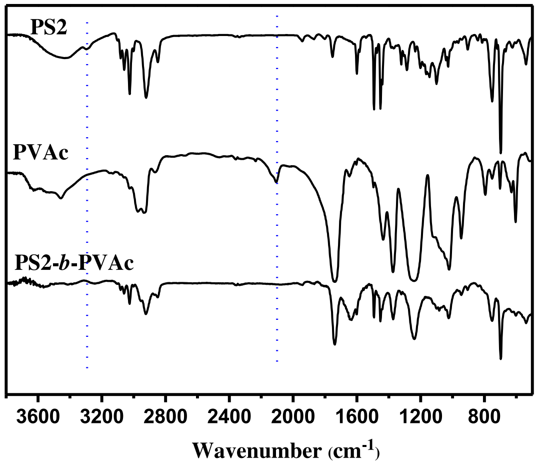


Fig. 4. FT-IR spectra of the homopolymers PS2 ($M_{n(GPC)} = 5000$ g/mol, $M_w/M_n = 1.12$), PVAc ($M_{n(GPC)} = 1800$ g/mol, $M_w/M_n = 1.19$) and copolymer PS2-*b*-PVAc ($M_{n(GPC)} = 6700$ g/mol, $M_w/M_n = 1.21$).

obtained block copolymer PS2-*b*-PVAc containing azobenzene moiety was characterized by ^{1}H NMR spectra, as shown in Fig. 3 (PS2-*b*-PVAc). Compared with the spectra of PS and PVAc, the spectrum of block copolymer showed both typical signals of PVAc and PS. The signals at around 3.02–3.16 ppm due to the alkyne group in the terminated PS were disappeared after "click" reaction. The characteristic signals corresponding to the phenyl protons of the azobenzene group and carbazole were still observed at around 7.70–8.30 ppm in block copolymer spectrum. All of these signals confirmed the structure of azobenzene-functionalized block copolymer PS2-*b*-PVAc. Moreover, the success of the "click" reaction can also be confirmed from FT-IR spectroscopy in Fig. 4. The signals at 3295 cm^{-1} (Fig. 4, PS2) and 2106 cm^{-1} (Fig. 4, PVAc) assigned to the alkyne and azide groups in PS2 and PVAc disappeared after the reaction. The FT-IR spectra indicated the high efficiency of the click reaction of PS2 and PVAc.

Thermal property of the polymers was evaluated by differential scanning calorimetry (DSC). All the polymers were heated or cooled with a heating/cooling rate of 10 °C min^{-1} under a continuous nitrogen flow. The second DSC heating curves of the homopolymers PS2, PVAc and copolymer PS2-*b*-PVAc were given in Fig. 5. The results showed typical glass transition temperature (T_g) of homopolymers PS2 and PVAc at 85 °C and 3 °C, respectively. Although PS and PVAc are immiscible [30], there only one glass transition point showed in block copolymer at 75 °C, which was between that of precursor homopolymer PS2 and PVAc. The reason may be due to the low molecular weight of PS and PVAc in the block copolymer [31]. No obvious phase separation occurs in current block copolymer.

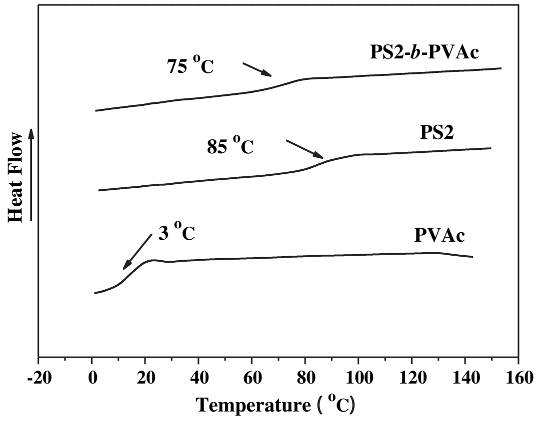
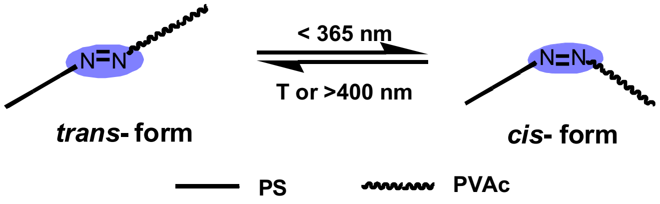


Fig. 5. Differential scanning calorimetry (DSC) of the homopolymers PS2 ($M_{n(GPC)} = 5000$ g/mol, $M_w/M_n = 1.12$), PVAc ($M_{n(GPC)} = 1800$ g/mol, $M_w/M_n = 1.19$) and copolymer PS2-*b*-PVAc ($M_{n(GPC)} = 6700$ g/mol, $M_w/M_n = 1.21$).



Scheme 4. Illustration of the *trans-cis-trans* isomerization process of block polymer PS2-*b*-PVAc.

3.4. Photo and thermal isomerization behaviors

Azobenzene polymers exhibited photo or thermal isomeriztion behavior, which undergoes conversion from *trans*- to *cis*-forms under the irradiation of 365 nm ultraviolet and reverse *cis*-to-*trans* forms under thermal energy in dark [32] (see Scheme 4). Thus, photoisomeriztion behavior of azobenzene-functionalized homopolymer PS2 and block polymer PS2-*b*-PVAc were studied in chloroform solution with the irradiation of 365 nm UV light. The thermal recovery behavior was investigated in the dark at 60 °C.

Firstly, the UV–vis absorption changes of block polymer PS2-*b*-PVAc after different period of UV irradiation were shown in Fig. 6 (A). The maximum absorption at 323.5 nm was the characteristic intense π–π* transition of azobenzene (*trans*-form) before UV exposure. Upon irradiation with 365 nm light, the *trans*-form of azobenzene changed to the *cis*-form (weak n–π* transition). The absorption maximum at 323.5 nm was quickly decreased, whereas the intensity of the weak *n*–π* transition band at about 450 nm increased slightly. However, the *trans*- form of the azobenzene did not completely disappear, which indicated the incomplete photoisomerization [33]. Similar characteristic behavior of homopolymer PS2 was also observed.

The photoisomerization kinetics of PS2-*b*-PVAc was plotted in Fig. 6 (b). The rate of *trans-cis* photoisomerization was analyzed from the absorption of 323.5 nm with different 365 nm light

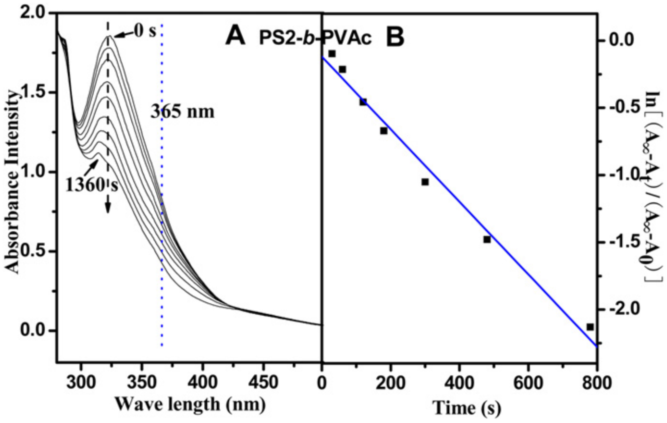


Fig. 6. (A): UV–vis absorption changes of block polymer PS2-*b*-PVAc with different irradiation time of 365 nm UV light; (B): First-order for *trans-cis* photoisomerization of block polymer PS2-*b*-PVAc. The concentration of the solution is 5.0 × 10^{-4} M in chloroform solution under different time interval at room temperature.

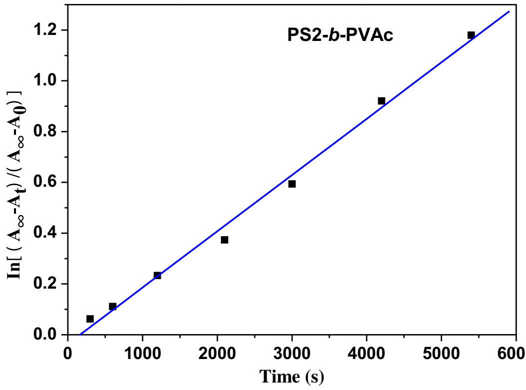


Fig. 7. First-order for thermal *cis-trans* isomerization of block polymer PS2-*b*-PVAc. The concentration of the solution is 5.0 × 10^{-4} M in chloroform solution under different time interval at 60 °C in the dark room.

irradiation time in chloroform solution. The first-order rate constants k_{exp} of photoisomerization was determined by Equation (3) [32]:

$$\mathrm{In}\left(\frac{A_\infty - A_0}{A_\infty - A_t}\right) = -k_{\mathrm{exp}}t \tag{3}$$

where A_∞, A_0 and A_t are absorbance at 323.5 nm after 365 nm light irradiation at infinite time, time zero and time *t*, respectively. The isomerization rate constants k_{exp} of PS2-*b*-PVAc was 0.0027 s^{-1}. According to this method, the k_{exp} of PS2 was 0.0047 s^{-1}, which was about nearly 2 times faster than that of PS2-*b*-PVAc, which was consistent with the result obtained in the literature [34]. The reason was considered due to sterically hindering effect of the polymer chain configuration.

Secondly, thermal *cis-trans* isomerization of the irradiated sample PS2-*b*-PVAc was investigated at 60 °C in dark room. The absorption at 323.5 nm was slowly restored to the initial state of PS2-*b*-PVAc at about 2 h, which means the equilibrium between *cis* and *trans* is established. The kinetics of the *cis-trans* thermal isomerizations of PS2-*b*-PVAc in dark were fitted satisfactorily to Equation (4):

$$\mathrm{Ln}\left(\frac{A_\infty - A_0}{A_\infty - A_t}\right) = k_{\mathrm{H}}t \tag{4}$$

where A_∞, A_0 and A_t are absorbance at 323.5 nm at time infinite, time zero and time *t*, respectively. The first-order *cis-trans* thermal isomerization was shown in Fig. 7. The *cis-trans* rate constant (k_{H}) of PS2-*b*-PVAc was 2.2 × 10^{-4} s^{-1}. These results confirmed that the isomerization of azobenzene in the polymer is reversible by the photo- and thermo procedures, which had a potential application in photochromic probes.

4. Conclusions

Well-defined block copolymers, poly(styrene)-*b*-poly(vinyl acetate), PS-*b*-PVAc containing middle azobenzene moiety were successfully synthesized by a combination of the reversible addition-fragmentation chain transfer (RAFT) and "click" chemistry. This novel method provided an efficient way to prepare terminal functionalized block copolymer: firstly, α-alkyne and azobenzene chromophore terminated poly(styrene) (PS), and ω-azido-terminated poly(vinyl acetate) (PVAc) were designed via RAFT technology. Secondly, "click" reactions were performed with the combination of CuBr and PMDETA as catalyst system. PS-*b*-PVAc block copolymers were demonstrated by GPC, ^{1}H NMR, FT-IR spectra and differential scanning calorimetry (DSC) analysis. Furthermore, the *trans-cis-trans* isomerization of PS-*b*-PVAc was also observed in chloroform solution. The k_e and k_{H} of PS-*b*-PVAc was 0.0027 and 2.2 × 10^{-4} s^{-1}, respectively.

Acknowledgments

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