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# Dynamic polymers containing one acylhydrazone linkage and dynamic behavior thereof

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#### ABSTRACT

Dynamic polystyrene (*d*-PS) and poly(*n*-butyl acrylate) (*d*-PBA) with an acylhydrazone linkage at each chain center were synthesized by atom transfer radical polymerization (ATRP) of corresponding monomers using a bis-bromoisobutyrate initiator bearing one acylhydrazone bond. Kinetic studies demonstrated that the polymerization followed a first-order mechanism. When treated with trifluoro-acetic acid or heated at 120 °C in solution, the polymer chains of *d*-PS and *d*-PBA were found to be cleaved partially into blocks of half original length, *i.e.* PS/2 and PBA/2, implying that a dynamic equilibrium of forming and breaking acylhydrazone bond was established.

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#### 1. Introduction

Recently dynamic covalent chemistry (DCC) [1] has attracted considerable attention as a powerful methodology for developing new materials with dynamic exchanged components [2-4]. Reversible covalent bonds, also called dynamic covalent bonds, play a key role in DCC to prepare such dynamic covalent polymers. In addition to normal properties of conventional polymers such as strength and stability, these dynamic polymers have shown the ability to exchange components between different polymer chains by stimuli-activating the exchange reaction of the dynamic covalent bonds [2-4]. This feature presents amazing opportunities to modify or control intrinsic properties of these dynamic polymers after formation [5–29]. Generally, dynamic covalent polymers were synthesized by polyaddition or polycondensation of small molecules [5-13,19,20,23] or polymer building blocks [25,26], or by chain growth polymerization of monomers with crosslinkers containing reversible covalent bonds [14-18,21,22,24]. Dynamic polymers containing acylhydrazone bonds [5,7,8,10,12,13,28], Diels-Alder cycloadduct [6,9], imines [25], alkoxyamine units [14-16,20-23], trithioesters [18,24] or disulfide bonds [19,27,29] were reported to reveal self-healing [17,18,24,27-29], mesh size control [14], tunable mechanical [10] or optical properties [11]. Moreover, block copolymers with dynamic covalent linkage as the junction of two segments have been recently reported for preparation of thin membranes with well-defined nanopores [25]. After selfassembled into nanostructured cylindrical morphology in thin films, the discontinuous cylindrical domains can be removed by cleaving the oxy-imine bonds to give the pores with functionalized walls. Dynamic polymers, polystyrene-*b*-poly(ethylene glycol) and polystyrene-*b*-polyisoprene, with H-bonding linkage as the junction of the two segments were also reported and demonstrated microphase separation like their covalent analogues [30].

Herein, we report synthesis and properties of well-defined homopolymers with a dynamic covalent linkage located at the chain center given by controlled radical polymerization. The synthetic route of the polymers is shown in Scheme 1. A covalent reversible acylhydrazone bond is incorporated in the initiator (compound 2, Scheme 1) for ATRP before polymerization. Kinetics of the ATRP of styrene and n-butyl acrylate were investigated, proving that the polymerizations were "living"/controlled ones. Such novel polymers demonstrated interesting equilibrium cleavage at dynamic linkages when treated with trifluoroacetic acid or heated at 120 °C in solution.

#### 2. Experimental

#### 2.1. Materials

CuBr was purified by washing crude chemical with acetic acid, absolute ethanol and diethyl ether, and then dried under vacuum. Chloroform, butyl acrylate (*n*-BA, Aldrich), N,N-dimethylformamide (DMF, Beijing Chemical Reagent Co.) and styrene (St, >99%, Beijing





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Scheme 1. Synthesis of functional initiator 2 and dynamic polymers d-PS and d-PBA.

Chemical Reagent Co.) were dried over calcium hydride for 24 h at room temperature and distilled before use. Triethylamine was dried by KOH. Tetrahydrofuran was dried by refluxing over Na prior to use. 2-Bromoisobutyryl bromide (98%, Aldrich), *N,N,N',N'',N''-*pentamethyl-diethylenetriamine (PMDETA, 99%, Aldrich), 2,2,2-trifluoro acetic acid (TFA, Beijing Xingjin Chemical Works), 4-hydroxy benzohydrazide (98%, Alfa Aesar) and other reagents were used as received without further purification.

#### 2.2. Measurements

Size exclusion chromatography (SEC) was composed of Waters 515 HPLC pump and Waters 2414 refractive index detector equipped with three Waters styragel columns HT2, HT4 and HT5. DMF with LiBr (1 g/L) was used as eluent at a flow rate of 1.0 mL/min at 50 °C. PS standards were used for the calibration. Nuclear magnetic resonance spectroscopy (NMR) spectra were recorded on a Bruker DMX400 spectrometer operated in the Fourier transform mode.  $d_6$ -DMSO was used as the solvent. Infrared spectra were recorded on a Nicolet AVA-TAR 330 FT-IR spectrometer.

#### 2.3. Polymer preparation

The synthetic routes of dynamic polymers are shown in Scheme 1.

#### 2.4. Preparation of compound 1

4-Hydroxybenzohydrazide (6.3 g, 41.4 mmol) and 4-hydroxybenzoaldehyde (5.0 g, 40.9 mmol) were dissolved in 150 mL of alcohol, and then refluxed for 8 h. After cooling to 4 °C for 4 h in refrigerator, white power was precipitated from alcohol and obtained by filtration. Yield 87%. <sup>1</sup>H NMR ( $\delta$ , ppm): 6.8 (d, 4H), 7.4(d, 2H), 7.8 (d, 2H), 8.2 (s, 1H), 9.9-10.1 (2H), 11.4 (s, 1H); mp 288–290 °C.

#### 2.5. Preparation of compound 2

Compound 1 (5.0 g, 19.5 mmol) and TEA (11.8 g, 117.0 mmol) were dissolved in 150 mL of THF, and then stirred at room

temperature for 30 min. After 2-bromoisobutyryl bromide (11.2 g, 48.7 mmol) was added into the mixture, the reaction was kept for 12 h. Then the solvent was evaporated, the crude product was dissolved in 100 mL of alcohol. After cooling to 4 °C for 4 h in refrigerator, white power was precipitated. The collected product was dried in vacuum for 48 h until constant weight. Yield 64%. <sup>1</sup>H NMR ( $\delta$ , ppm): 1.9 (s, 12H), 7.3(d, 4H), 7.9-8.1 (d, 4H), 8.6 (2H), 12(s, 1H); mp 243–244 °C; Element analysis: Calcd for C22H22Br2N2O5: C 47.68, H 4.00, N 5.05. Found: C 47.68, H 4.11, N 5.04.

#### 2.6. Preparation of polystyrene d-PS<sub>750</sub>

The *d*-PS<sub>750</sub> was prepared by atom transfer radical polymerization (ATRP) of styrene (St): Initiator **2** (10 mg, 18 µmol), PMDETA (7.8 µL, 36 µmol), St (7.51 g, 72.1 mmol) and DMF (0.1 mL) were charged into a Schlenk tube. The mixture was degassed by three freezes—evacuate—thaw cycles and backfilled with nitrogen. As soon as CuBr (5.2 mg, 36 µmol) was introduced, the tube was vacuumed and flame-sealed. Polymerization was carried out in an oil bath thermostated at 65 °C for 36 h, and then the reaction mixture was exposed to the air and diluted with THF. After passing through an alumina column and removing the solvents on a rotary evaporator, the residues were precipitated into an excess of methanol and purified by repeat precipitation. The final product *d*-PS<sub>750</sub> was dried under vacuum over night.

#### 2.7. Preparation of poly(n-butyl acrylate)s d-PBA<sub>100</sub> and d-PBA<sub>234</sub>

The *d*-PBA<sub>100</sub> was prepared by ATRP of butyl acrylate (*n*-BA): Initiator **2** (100 mg, 181  $\mu$ mmol), PMDETA (78  $\mu$ L, 360  $\mu$ mol), *n*-BA (4.53 g, 36.2 mmol) and DMF (0.1 mL) were charged into a Schlenk tube. The mixture was degassed by three freezes–evacuate–thaw cycles and backfilled with nitrogen. As soon as CuBr (52 mg, 360  $\mu$ mol) was introduced, the tube was vacuumed and flame-sealed. Polymerization was carried out in an oil bath thermo-stated at 65 °C for 36 h, and then the reaction mixture was exposed to the air and diluted with THF. After passing through an alumina column and removing the solvents on a rotary evaporator, the residues were precipitated into an excess of mixture of methanol



**Fig. 1.** <sup>1</sup>H NMR spectra of compound **1** and **2** in  $d_6$ -DMSO.

and water (v/v = 1:1) and purified by repeat precipitation. The final product *d*-PBA<sub>100</sub> was dried under vacuum over night.

For *d*-PBA<sub>234</sub>: Initiator **2** (50 mg, 90.5 μmol), PMDETA (39 μL, 180 μmol), DMF (0.1 mL), *n*-BA (4.53 g, 36.2 mmol) and CuBr (26 mg, 180 μmol).

#### 2.8. Acidolysis of d-PBA<sub>234</sub>

The *d*-PBA<sub>234</sub> (20 mg) and DMF (1 mL) were charged into a centrifugal tube. After TFA (50  $\mu$ L) was added and mixed homogenously, the solution was checked by SEC at different time.

#### 2.9. Pyrolysis of d-PBA<sub>234</sub>

The *d*-PBA<sub>234</sub> (200 mg) and DMF (10 mL) were charged into a 25 mL flask. Pyrolysis was carried out in an oil bath thermostated at 120  $^{\circ}$ C. The solution was checked by SEC at different time.

#### 3. Results and discussion

#### 3.1. Preparation of d-PS and d-PBA

Compound **2** containing an acylhydrazone bond and two 2bromoisobutyrate groups was used as an initiator for ATRP in this



Fig. 2. FT-IR spectra of (a) compound 1 and (b) compound 2.



**Fig. 3.** Kinetic plot of the polymerization of St initiated from compound **2** by ATRP at 65 °C in DMF, **[2]**:[St]:[CuBr]:[PMDETA] = 1:200:2:2.  $V_{DMF}$ : $V_{St}$  = 1:6.



**Fig. 4.** Kinetic plot of the polymerization of *n*-BA initiated from compound **2** at 65 °C in DMF, [**2**]:[*n*-BA]:[CuBr]:[PMDETA] = 1:200:2:2. V<sub>DMF</sub>:V<sub>n-BA</sub> = 1:6.

study, and its structure and synthetic method are shown in Scheme 1. <sup>1</sup>H NMR spectra of compound 1 and 2 (Fig. 1) show that the two peaks at 10.1 ppm at 9.9 ppm from the aromatic –OH groups of compound 1 in curve A are invisible in curve B, while one peak at 2.1 ppm from the –CH<sub>3</sub> groups of compound 2 is observed in curve B. In FT-IR spectra (Fig. 2) of compound 1 and 2, the absorption peaks of carbonyl group from compound 1 and 2 appear at  $1639 \text{ cm}^{-1}$  and  $1653 \text{ cm}^{-1}$  respectively. The peak at  $1755 \text{ cm}^{-1}$  (in curve b) is ascribed to the carbonyl group of the ester in compound 2. All the results prove that compound 2 was prepared successfully.

Homopolymers, d-PS and d-PBA, were synthesized by ATRP with the initiator **2** (Scheme 1). Fig. 3 shows ATRP of St in DMF at 65 °C

Table 1	
Synthesis of <i>d</i> -PS and <i>d</i> -PBA initiated by <b>2</b> .	

Entry	Feed ratio <sup>a</sup>	Monomer	Time (h)	$M_{\rm n}({\rm kDa})^{\rm b}$	PDI <sup>b</sup>	Yield (%)
d-PS <sub>750</sub>	1:4000:2:2	St	36	78	1.23	15 <sup>c</sup>
d-PBA100	1:200:2:2	n-BA	7	12.5	1.1	50 <sup>d</sup>
d-PBA <sub>234</sub>	1:400:2:2	n-BA	8	29.9	1.14	58.5 <sup>d</sup>

<sup>a</sup> [2]:[M]:[CuBr]:[PMDETA], 65 °C.

<sup>o</sup> Given by SEC (DMF system) calibrated by polystyrene standards.

<sup>c</sup> Given by weighting method.

<sup>d</sup> Given by <sup>1</sup>H NMR by comparing the protons of monomers and polymers in the reaction mixture.



**Fig. 5.** (A) SEC traces of *d*-PBA<sub>234</sub> in DMF solution (20 mg/mL) mixed with TFA (1/60, v/v) for different time at room temperature (a: 0 h; b: 6 h; c: 12 h; d: 47.5 h; e: 72 h; f: 84 h; g: 95 h); (B) Decomposed *d*-PBA<sub>234</sub> for different time.

and the plot of ln ( $[M]_0/[M]$ ) against polymerization time is linear and the conversion of St increases with increasing polymerization time. Similarly, ATRP of *n*-BA was carried in DMF at 65 °C and its kinetic is shown in Fig. 4. The plot of ln ( $[M]_0/[M]$ ) against polymerization time in Fig. 4 is also linear. As shown in Fig. 3,  $M_w/M_n$ (PDI) of *d*-PS formed during the polymerization process increased gradually from 1.14 to 1.42, indicating the radical coupling termination occurred. For *d*-PBA system in Fig. 4, the PDI is 1.07–1.10, demonstrating no obvious termination. All the results indicated that the polymerizations initiated by **2** are controlled. Thus, we prepared several samples, *d*-PS<sub>750</sub>, *d*-PBA<sub>100</sub> and *d*-PBA<sub>234</sub>, for further investigation, and the results were shown in Table 1.

## 3.2. Dynamic behavior of *d*-PBA under acid environment or at high temperature

It is known that acylhydrazone bond is reversible under a mild acidic condition [31]. Polyacylhydrazones formed by condensation of small monomers were found to reversibly exchange their monomeric units under acidic and heating conditions after formation [13]. In this study the polymer d-PBA<sub>234</sub> was chosen for acidolysis investigation in DMF solution (polymer concentration 20 mg/mL) at room temperature. When TFA (1/60, v/v) was added to the solution, the acylhydrazone linkage at the central point of d-PBA234 chain was activated and gradually decomposed into acylhydrazine and aldehyde groups, thus generating half polymer chains PBA<sub>234</sub>/2. Since the acid is also a catalyst to form acylhydrazone linkage, the reverse process of reforming d-PBA234 by condensation of the acylhydrazone and aldehyde groups at the ends of PBA234/2 was also active. Therefore, an equilibrium between the *d*-PBA<sub>234</sub> and its cleaved products PBA<sub>234</sub>/2 should be gradually established. As monitored by SEC at different time (Fig. 5A), the peak of *d*-PBA<sub>234</sub> (curve a) was at elution time 26.5 min, and its intensity decreased along with increasing acidolysis time (curve b to g in Fig. 5A). Meanwhile, another peak appeared at about 27.7 min with hydrolysis and then increased rapidly. Since the latter peak had a half molecular weight, it is ascribed to the hydrolyzed product PBA<sub>234</sub>/2. The relative amount of remained *d*-PBA<sub>234</sub> and produced PBA<sub>234</sub>/2 was determined by comparing their individual peak areas after deconvolution in the SEC curves and then the percentage of decomposed *d*-PBA<sub>234</sub> with different acidolysis time (Fig. 5B) was calculated based on the ratio: [the peak area of PBA<sub>234</sub>/2]/[the area of whole trace]  $\times$  100%. The results show that the amount of cleaved *d*-PBA<sub>234</sub> increased with increasing acidolysis time and reached to 77% after 95 h. The decomposing rate of the acylhydrazone linkage was fast in 6 h and then it slowed down, indicating that the decomposing and the reforming reactions of the acylhydrazone bond between d-PBA<sub>234</sub> and PBA<sub>234</sub>/2 were built gradually.

Without acid catalyst, the exchange reaction between acylhydrazone and acylhydrazine/aldehyde also occurred but with much less efficient at 120 °C [12]. Dynamic behaviors of the polymer *d*-PBA<sub>234</sub> at high temperature without acid catalyst were further investigated here. As shown in Fig. 6, *d*-PBA<sub>234</sub> in DMF solution (20 mg/mL) gradually decomposed to 72.6% after pyrolysis at 120 °C for 7 d. The decomposing rate was fast in the first one day and then slowed down gradually. Apparently, *d*-PBA<sub>234</sub> decomposed slower under pyrolysis conditions than under acidic conditions at mild temperature, which is in agreement with the exchange efficiency of polyacylhydrazones in literature [12]. Because pyrolysis needs no outside additive chemicals, it may be useful to trigger segment exchange by heating.

Estimated by extrapolation in Figs. 5B and 6B, about 20% of *d*-PBA<sub>234</sub> may be presented when the equilibrium is built. Namely it



Fig. 6. (A) SEC traces of *d*-PBA<sub>234</sub> in DMF solution (20 mg/mL) heated for 120 °C at different time (a: 0 d; b: 1 d; c: 2.5 d; d: 3 d; e: 4 d; f: 5 d; g: 6 d; h: 7 d); (B) Decomposed *d*-PBA<sub>234</sub> for different time.

took a very long time to build the equilibrium for cleavage and reformation. This result contrasted to the case of small hydrazones formed by hydrazine derivatives bearing electron withdrawing groups and aromatic aldehydes. Under close to neutral conditions (6 < pH < 8) in water, formation and hydrolysis of these small hydrazones is very rapid, taking several minutes to hours to reach an equilibrium [32]. From the decomposing ratio curve of *d*-PBA<sub>234</sub> in Fig. 6B, it can be seen that an equilibrium was not reached even after 7 days at 120 °C. This slow rate to reach an equilibrium should be attributed to the macromolecular tails tethered to the dynamic linkage.

#### 4. Conclusions

Dynamic polymers *d*-PS and *d*-PBA containing one dynamic acylhydrazone linkage located in the chain center were prepared by ATRP. The dynamic acylhydrazone linkage was introduced in the initiator before polymerization. Kinetic studies indicated that the polymerizations initiating by the initiator are "living"/controlled ones. These dynamic polymers were partially cleaved into halves of their original chain length when treated with trifluoroacetic acid or heated at 120 °C in solution, indicating an equilibrium between polymers through the formation and scission of the acylhydrazone bond was established although it took more time than that of small molecules.

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