



# 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 trifluoroacetic 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 self-assembled 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.

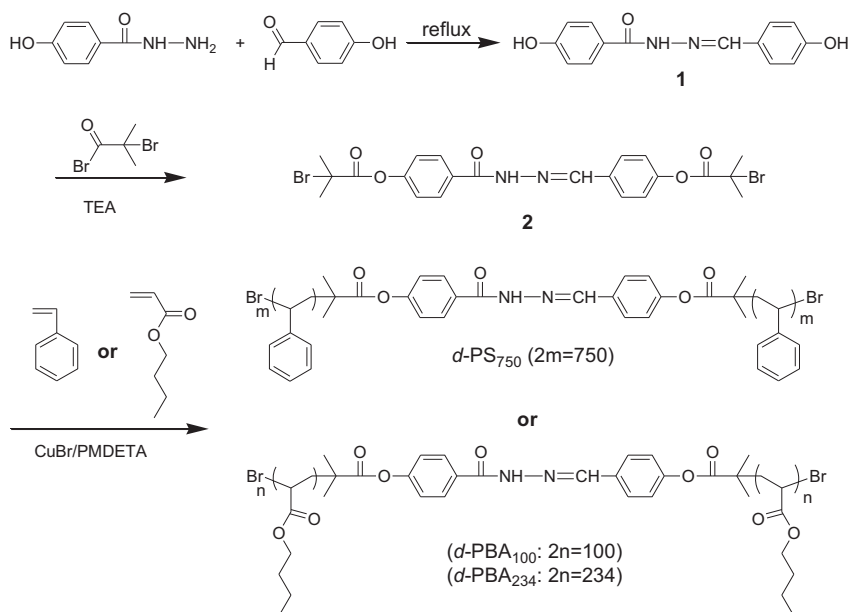
## 2. Experimental

### 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-trifluoroacetic acid (TFA, Beijing Xingjin Chemical Works), 4-hydroxybenzohydrazide (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*<sub>6</sub>-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-hydroxybenzaldehyde (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 powder was precipitated from alcohol and obtained by filtration. Yield 87%. <sup>1</sup>H NMR (δ, 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 powder was precipitated. The collected product was dried in vacuum for 48 h until constant weight. Yield 64%. <sup>1</sup>H NMR (δ, 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 C<sub>22</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>5</sub>: 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 μmol), PMDETA (78 μL, 360 μmol), *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 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 mixture of methanol

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