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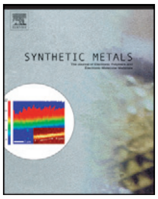

Photo-tunable multi-arm star azobenzene side-chain polymer with hyperbranched polyether core

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ABSTRACT

A hyperbranched polymer containing azo chromophore groups on the periphery has been successfully synthesized by atom transfer radical polymerization using hyperbranched polyester bearing peripheral bromoacetyl groups as the initiator and 4-[(*E*)-phenyldiazenyl]phenyl acrylate as monomer and CuBr/2,2′-bipyridine (bpy) as the catalyst. The resultant products were characterized by FT-IR, NMR, TEM, and EA. The photo-tunable azobenzene-functionalized hyperbranched polymer as well as the corresponding azo monomer showed photoresponsive behavior of the azobenzene type molecules. UV–vis spectra of the azobenzene-functionalized hyperbranched polymer in tetrahydrofuran showed isomerization of azobenzene units upon irradiation with UV (365 nm).

1. Introduction

Over the past decade, the field of non-linear polymers such as dendritic or hyperbranched macromolecules has attracted considerable attention because of their specific architecture and unique properties [1–3]. Such desirable properties include high solubility, low viscidity, high density of surface functional groups and special encapsulating microenvironment at the core compared to linear analogues. These attractive features have led to developing various synthetic routes to those polymers [1,4]. In many case, the hyperbranched polymer are discussed as a more economical replacement of dendrimers in many applications because of their easier preparation.

Side-chain liquid crystalline polymers (LCPs), which represent a combination of liquid crystalline behavior and polymeric properties, have been the subject of intensive research during the last decade. Side-chain LCPs have been studied and optimized for a wide range of applications such as optical data storage, non-linear optics, stationary phases for gas chromatography, supercritical-fluid chromatography and high-performance liquid chromatography, solid polymer electrolytes, separation membranes and display materials [5,6]. Many linear side-chain liquid crystalline block copolymers have been synthesized by different living polymerization [7,8], such as controlled/“living” radical polymerizations including atom transfer radical polymerization (ATRP) [9–12], and reversible addition-fragmentation chain transfer (RAFT) [13], and nitroxide-mediated radical polymerization (NMP) [14,15]. For example, Gopalan et al. have synthesized and characterized rod-coil diblock, triblock, and starblock copolymers of controlled molecular weight by stable free radical polymerization, where the rod part consists of “mesogen jacketed liquid crystalline segments” (MJLCP) [15].

Dendrimers with photoresponsive azobenzene chromophores in the exterior [16,17], interior [18], and throughout the dendritic architecture [19], or hyperbranched polymers with photoresponsive azobenzene chromophores [20–22] have been designed and prepared recently. Jin and his research team reported 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 ATRP [22]. Especially, the incorporation of azo moieties in dendrimers or hyperbranched polymers can potentially widen the application of non-linear polymers in areas such as photoresponsive materials for self-assembly and encapsulation.

In this work, we report the synthesis of a novel photoresponsive azobenzene-functionalized hyperbranched polymer based on a precursor hyperbranched polyester by ATRP. The hyperbranched macroinitiator was synthesized from hyperbranched polyesters (HP3) esterified with bromoacetylbromide. It was used for the atom transfer radical polymerization of 4-[(*E*)-phenyldiazenyl]phenyl

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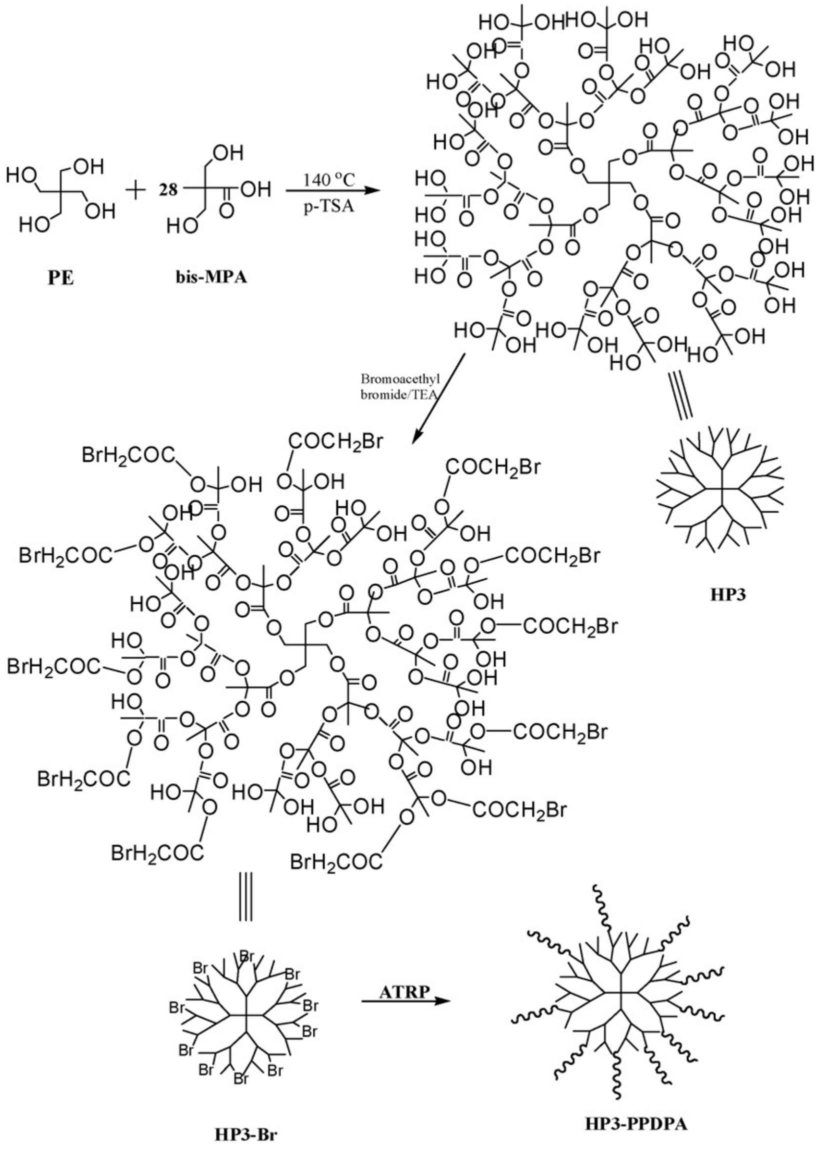

Scheme 1. Reaction scheme for synthesis of hyperbranched polyester and star-shaped hyperbranched polyester-cored poly (4-[(*E*)-phenyldiazenyl]phenyl acrylate).

acrylate in the presence of CuBr as catalyst and bpy as ligand in DMF. The synthetic process to the ideal structure of the photoresponsive azobenzene-functionalized hyperbranched polymer is presented in Scheme 1.

2. Experimental details

2.1. Materials

Pentaerythritol (PE), 2,2-dimethylol propionic acid (bis-MPA) and *p*-toluenesulfonic acid (*p*-TSA) used were all analytical grade and were used as received from Tianjin Chemical Co. (Tianjin, China).

Bromoacetylbromide was of analytical reagent grade from Acros Organics (Phillipsburg, NJ, USA). CuBr (Tianjin Chemical Co., Tianjin, China) was analytical reagent grade was purified by stirred in glacial acetic acid, filtered, washed with ethanol and dried. 2,2′-Bipyridine (bpy) (A.R., 97.0%) provided by Tianjin Chemical Co., China was recrystallized twice from acetone. Triethylamine (TEA) (A.R., 99.0%) was dried by CaH_2 overnight, and then distilled under reduced pressure before use. Tetrahydrofuran (THF), ethanol, *N*,*N*-dimethylformamide (DMF) and other solvents used were all of analytical reagent grade from Tianjin Chemical Co., China, and were used without further purification.

2.2. Synthesis of 4-hydroxyazobenzene

The preparation of 4-hydroxyazobenzene was carried out by a reaction between aniline and phenol according to literature [23] (Scheme 2). ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 6.8–8.0 (9H, **phenyl**); 5.0 (1H, –Ar–**OH**).

2.3. Synthesis of 4-[(E)-phenyldiazenyl]phenyl acrylate (PDPA)

4-[(*E*)-Phenyldiazenyl]phenyl acrylate was prepared by the condensation reaction of 4-hydroxyazobenzene and acryloyl chloride in THF, in the presence of TEA to trap HCl. 4-Hydroxyazobenzene (10 g, 0.05 mol) was dissolved in 100 mL THF in a 250 mL flask, to