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Structural characterization and thermal behavior of dendritic-linear PGMA-HPAM-r-PS copolymers in a self-assembled microporous matrix

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ABSTRACT

A series of dendritic-linear copolymers, composed of poly(glycidyl methacrylate-grafted- 3,3′-dimethyl-(4-hydroxyphenylazanediyl) bis(2-methylpropanoate))-random-polystyrene (PGMA-HPAM-r-PS), were successfully synthesized via a macromonomer route. Characterization of the copolymers and investigation of their thermal behavior revealed a significant influence of the dendritic GMA-HPAM segment. The thermal degradation temperature (T_d) of the dendritic-linear PGMA-HPAM-r-PS copolymer was elevated as the weight percentage of dendritic segment (GMA-HPAM) increased. The glass transition temperatures of the copolymers exhibited a strong, complex dependence on the dendritic GMA-HPAM segment, with three behavioral ranges. DSC data were attributed to two distinct effects of the dendritic segment: (i) the effect of the dendritic segment grafting on copolymer chains, and (ii) intermolecular interactions between the dendritic and styrene segments. Microporous dendritic-linear PGMA-HPAM-r-PS copolymer matrices were prepared using solvent-induced phase separation at room temperature. The self-assembled surface morphology was affected by (i) the micellar domains of the dendritic and styrene segments and (ii) inter- and intramolecular interactions between the dendritic and styrene segments. An interesting relationship between thermal behavior and surface morphology was discovered, which can provide a simple, accurate and rapid means of finding the optimum dendritic segment content for producing a hexagonally ordered microporous matrix for different dendron generations.

1. Introduction

To obtain novel physical and chemical properties of macromolecules, polymer synthesis has rapidly developed for linear, block, hyper-branched, and, in particular, dendritic copolymers. Dendritic macromolecules [1–3] have recently attracted significant attention due to their various functions and properties. Dendritic macromolecules, known as dendrimers, were first successfully synthesized by Vögtle [4], Denkewalter [5,6], and Tomalia et al. [7,8]. Dendritic macromolecules can be synthesized by both divergent [7,9] and convergent [10–12] methods to form distinct three-dimensional structures with unique physical and chemical properties [13–17], such as low intrinsic viscosity, high solubility, high miscibility, and high reactivity. Dendritic segments have consequently been appropriated in many studies to construct 3-D functional copolymers [18–20].

The branched structure and functionality of the dendritic segment alter the properties of the dendritic copolymers significantly when compared to linear ones. The self-assembling structure of dendritic-linear copolymers, both in bulk and in solution, shows that the dendritic segment affects the phase boundary and thus enhances phase separation [21–23]. Dendritic copolymers have potential applications in electronic and optical devices [24–26], catalytic supports [27] and biosensors [28]. They have been widely used in recent years as templates for preparing microporous thin films with ordered structures [29–33], such as hexagonally structures which were formed due to phase separation and self-assembling of copolymers. Dendritic macromolecular chemistry and physics therefore hold promise for various applications in the field of materials science.

The main challenges in the synthesis of dendritic copolymers are as follows: (1) steric repulsion resulting in incomplete reactions; (2) autocatalytic decomposition of sensitive dendrons due to exceptionally high functional group density; (3) high molar

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mass and occasionally large differences in the molar mass reactants, which make it difficult to achieve the desired stoichiometric ratios; and (4) purification of high molar mass reactants. There are three main synthetic routes for dendritic copolymers: "grafting-through" (macroinitiator), "grafting-onto", and "macromonomer". The macromonomer route has an obvious advantage over the other two strategies in that it does not involve a post-polymerization reaction and it can offer precise control over the dendritic side group [34].

Recently, we used the macromonomer route to synthesize a series of dendritic-linear copolymers, namely, poly(glycidyl methacrylate-grafted- 3,3′-dimethyl-(4-hydroxyphenylazanediyl) bis(2-methylpropanoate))-random-polystyrene (PGMA-HPAM-r-PS). We also used solvent-induced phase separation to construct hexagonally ordered microporous matrices [35]. This work shows that the domain for micellar formation and segment–segment interactions of the dendritic-linear copolymer control the surface morphology of the matrix. We have also confirmed that the appropriate macromonomer content can be tailored to promote self-assembly, forming a honeycomb-ordered microporous copolymer matrix. Lots of studies [29–33] focused on using the different routes to synthesize dendritic-linear copolymers and discussed upon their self-assembling behaviors by various inducing methods. It is hard to justify the formation of self-assembling structure, particularly at which dendritic content, without the use of inducing process. In our preliminary study, we that observed the self-assembling behavior appears to be in closed relation to the thermal properties of the PGMA-HPAM-r-PS copolymer. To elucidate the relationship between self-assembly and thermal properties, we carefully synthesized a dendritic-linear copolymer, PGMA-HPAM-r-PS, comprising of higher dendron generations. Investigation of the thermal behavior and structure of the dendritic-linear copolymer revealed the role of the dendritic GMA-HPAM segment content in the incorporation of a hexagonally ordered microporous matrix directly into a system of different generations of dendrons.

2. Experimental section

2.1. Materials

Ethylenediamine (EDA) (Fluka Co. Ltd.) and *p*-aminophenol (Aldrich Co. Ltd.) were used as received without further purification. In order to remove the inhibitors, styrene, methyl methacrylate (MMA), and glycidyl methacrylate (GMA) (Merck Co. Ltd.) were purified by distillation under reduced pressure. They were stored at 5 °C before use.

2.2. Polymerization procedure for the dendritic-linear copolymer

2.2.1. Synthesis of the 3,3′- dimethyl-(4-(2-hydroxy-3-(methacryloyloxy) propoxy) phenylazanediyl)bis(2-methylpropanoate) (GMA-HPAM) macromonomer

Synthesis of the dendron 3,3′-dimethyl-(4-hydroxyphenylazanediyl) bis(N-(2-aminoethyl)-2- methylpropanamide) (HPAM) has been demonstrated in previous work [35]. A solution of freshly distilled MMA in methanol was added dropwise to a *p*-aminophenol solution, in a nitrogen atmosphere, over a 2 h period. The resulting mixture was then stirred for 1 h at 0 °C. Following 5 days of stirring at room temperature and solvent removal from the mixture, a reddish-brown oil (HPAM-G1) was obtained. Next, a solution of HPAM-G1 precursor in methanol was carefully added to a vigorously stirred EDA solution in an ice bath at 0 °C, which was then stirred for 5 days at room temperature. Extraction with toluene yielded an amine-terminated product (HPAM-G1.5).

A solution of MMA in methanol was added dropwise to a solution of HPAM-G1.5 precursor in a nitrogen atmosphere over a 2 h period, followed by stirring for 1 h at 0 °C. The mixture was stirred at room temperature for 5 more days. This purification process yielded HPAM-G2 as the final product. The intended product with higher HPAM dendron generations was obtained by repetition of the previous procedure.

Next, the HPAM-G2 dendron solution was added to a glycidyl methacrylate (GMA) solution at 0 °C. The mixture was stirred for 12 h at room temperature, followed by extraction of by-products and excess dendrons, producing the dendritic macromonomer of GMA-HPAM in the form of a transparent orange oil.

2.2.2. Synthesis of the dendritic-linear copolymer

A mixture of initiator, azobisisobutyronitrile (AIBN), and styrene monomer in N, N-dimethylacetamide was placed in a three-neck 250-mL round-bottom flask. A solution of GMA-HPAM macromonomer in N, N-dimethylacetamide was added dropwise to the solution in the flask while mixing well under a nitrogen purge system. The mixture was then stirred for 1 h at room temperature before being heated to 80 °C for 48 h. Finally, the dendritic-linear copolymers (PGMA-HPAM-r-PS) were precipitated in methanol solution, separated by filtration, and then dried in a vacuum oven. The complete preparation procedure is illustrated in Scheme 1.

2.2.3. Preparation of PGMA-HPAM-r-PS copolymer films

Microporous films were cast in a glove box under a nitrogen atmosphere. The process took place at room temperature using 30 wt% PGMA-HPAM-r-PS copolymer solution in tetrahydrofuran (THF) and casting onto a variety of substrates, including glass slides, aluminum plates, metal wafers, and mica.

2.3. Characterization

The molecular weight and molecular weight distribution of the raw samples were determined by gel permeation chromatography (GPC) using a Postnova 1021 solvent delivery pump, a Viscotek 270 dual detector, a Viscotek VE 3580 RI detector, and American Polymer Standards Corporation 10 μm AM Gel GPC columns (AM Gel 10^3 Å, 10^4 Å, and 10^5 Å) with linear polystyrene (PS) standards. THF (HPLC grade) was used for elution at a flow rate of 1 mL/min. The GPC results were calibrated using conventional calibration methods (CC). ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker 400-MHz FT-NMR instrument; chemical shifts were recorded in parts per million using tetramethylsilane as an internal standard. Fourier transfer infrared (FT-IR) spectra were recorded with a Varian 2000 FT-IR analyzer operating from 700 to 4000 cm^{-1} at room temperature. Spectra were obtained using a resolution of 4 cm^{-1} and were averaged over 32 scans. The samples were mixed thoroughly with approximately 3 wt% potassium bromide (KBr), and the resulting powders were pressed into a transparent pellet. Elemental analysis (EA) was performed using an Elementar Vario EL III elemental analyzer. The thermal properties of the polymers were measured by thermogravimetric analysis (TGA) using a TA TGA-Q50 thermogravimetric analyzer. Samples were heated from room temperature to 800 °C at a heating rate of 20 °C/min under a nitrogen purge system. TGA-FTIR studies were performed using a TA TGA-Q50 thermogravimetric analyzer, which was interfaced to a Varian 2000 FTIR spectrometer. T_g for the copolymers was determined by DSC, from the midpoint of the inflection tangent, after heating the samples a second time at 10 °C/min. TGA and DSC data were analyzed using TA Instruments Universal Analysis software. A Hitachi S4200 field emission scanning electron microscope (FE-SEM) was used to observe the morphology of the dendritic-linear PGMA-HPAM-r-PS copolymer.