Contents lists available at ScienceDirect

Polymer

Self-assembly of hydrogen-bonded comb copolymer complexes of poly(p-hydroxystyrene) and 4-alkylpyridine amphiphiles

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ARTICLE INFO

ABSTRACT

The self-assembly of the hydrogen-bonded complexes between poly(p-hydroxystyrene) (PpHS) and 4-alkylpyridine amphiphiles is studied using infrared spectroscopy, differential scanning calorimetry, polarized optical microscopy, transmission electron microscopy and small- and wide-angle X-ray scattering. Interesting differences are observed with the well-studied inverted system of poly(4-vinylpyridine) and alkylphenol amphiphiles. When the alkyl tails of the 4-alkylpyridine amphiphiles are long enough, 19 and 21 respectively, an ordered lamellar structure is formed on cooling where the ordering and crystallization of the alkyl tails occur quasi simultaneously. For a shorter alkyl tail of length 17 no ordered structure is formed. This is quite different from the inverted P4VP/alkylphenol systems, where already for an alkyl tail of length 15, i.e., pentadecylphenol, an ordered structure is formed below ca. 55 °C, followed by crystallization of the alkyl tails at ca. 20 °C. This can be attributed to the possibility of (intramolecular) hydrogen bond formation of PpHS.

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1. Introduction

The combination of supramolecular principles with block copolymer self-assembly [18,19,26] has proven to be a very promising concept in nanotechnology [1–5]. In particular, comb-shaped supramolecules formed by amphiphilic side chains noncovalently attached to a linear polymer backbone, have been studied in depth theoretically as well as experimentally. Physical interactions, such as ionic interactions [6,7], coordination bonding [8], and hydrogen-bonding [1], can be used to prepare such supramolecular structures. Of these, hydrogen-bonding appears to be the most promising as it results in materials that can be manipulated relatively easily by external stimuli, temperature in particular [5,9]. Besides homopolymers [5,10,15], di- [5,17,45], and triblock copolymers [11] have been used so far.

The characteristic length scale of the self-assembled structures as well as the structure itself can easily be manipulated varying the amount of low molecular component. After the self-assembled structure desired is obtained there is the additional possibility to remove the low molecular weight amphiphiles by dissolving in a suitable solvent [12]. This concept has been extensively pursued by Stamm and co-workers using PS-b-P4VP diblock copolymers in combination with 2-(4-hydroxybenzeneazo)benzoic acid to create nanoporous thin films [13,14]. We studied other hydrogen bond accepting polymers besides P4VP as well [17] and used PDP-based supramolecular block copolymer bulk samples exhibiting a large-length-scale bicontinuous gyroid morphology [21] to create continuous nanoporous polymeric structures, which were used as templates to produce, e.g., metallic nickel nanofoams [16,20,46].

Various systematic studies of the bulk phase behavior of hydrogen-bonded comb-shaped supramolecules were reported [1,5,10,15,17,22–25]. Self-assembly in the melt of complexes consisting of pentadecylphenol (PDP) hydrogen-bonded to homopolymer poly(4-vinylpyridine) (P4VP) was studied via Infrared studies (IR) and showed that the hydrogen-bonding is fairly complete for stoichiometric compositions (i.e., one PDP molecule per pyridine group), when the temperature is below 100 °C [23,27]. Temperature dependent small-angle X-ray scattering (SAXS) showed that under stoichiometric conditions there is an order-disorder transition (ODT) in P4VP(PDP) at about 65 °C when cooling from a high-temperature isotropic state [10]. The resulting microphase-separated lamellar morphology consists of nonpolar alkyl tails segregated from the polar P4VP/phenol complex. The alkyl tails

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crystallize around room temperature. If the temperature is increased above the ODT a characteristic correlation hole peak is present at a position and with a height depending on the fraction of hydrogen bonds [28]. The combination of block copolymers of P4VP and polystyrene (PS) with PDP resulted in the well-known structure-in-structure morphologies, which were systematically imaged by transmission electron microscopy (TEM) [29].

Recently, *tert*-butoxystyrene (*t*BOS) was used in our group in the synthesis of P*t*BOS-*b*-P4VP dicblock copolymer [30], P*t*BOS-*b*-PS-*b*-P4VP triblock copolymers [11] and PS-*b*-(P*t*BOS-*b*-PS)$_n$-*b*-P*t*BOS multiblock copolymers [31]. In order to obtain self-assembled structures with the latter multiblock copolymers, the *tert*-butyl ether was hydrolyzed to result in poly(*p*-hydroxystyrene) (P*p*HS). Because *p*-hydroxystyrene has a much more unfavorable interaction with styrene than *tert*-butoxystyrene, the PS-*b*-(P*p*HS-*b*-PS)$_n$-*b*-P*p*HS multiblock copolymers synthesized showed interesting two-length-scale phase behavior [31]. Because P*p*HS can also be used as a proton donor for hydrogen-bonding a third length scale may conceptually be introduced if P*p*HS is combined with suitable amphiphiles such as, alkylpyridine amphiphiles. In that case a supramolecular system is obtained that is similar to the P4VP/PDP hydrogen-bonded complexes described above with the subtle difference that the pyridine group is now part of the amphiphile whereas the phenol group is attached to the backbone of the polymer, as depicted in Scheme 1. If this concept works, the use of PS-*b*-P*p*HS diblock copolymers will result in all the possibilities discussed before for the PS-*b*-P4VP systems, except that after removing the alkylpyridine amphiphiles nanoporous systems will be obtained with pores covered with hydroxyl rather than pyridine groups.

In the present paper, the self-assembly of hydrogen-bonded comb copolymer complexes of poly(*p*-hydroxystyrene) and 4-alkylpyridine amphiphiles is investigated using homopolymer poly(*p*-hydroxystyrene) (P*p*HS).

The hydrogen-bonding between the pyridine group of C$_{21}$Py and the phenol group of P*p*HS was investigated via FTIR spectroscopy in which the samples varied in amphiphile mole fraction x ($x = 0.5$, 1.0, and 1.5). Here, x represents the ratio between the pyridine groups of the amphiphile and the phenol groups of the polymer. Furthermore, the different supramolecular complexes formed between P*p*HS and C$_{17}$Py ($x = 1.0$), C$_{19}$Py ($x = 1.0$), and C$_{21}$Py ($x = 0.5$, 1.0, and 1.5) were investigated with differential scanning calorimetry (DSC) and simultaneous small (SAXS) and wide (WAXS) angle X-ray scattering during cooling from the melt. The results are compared with the thoroughly investigated P4VP/PDP supramolecular system and the differences observed are discussed.
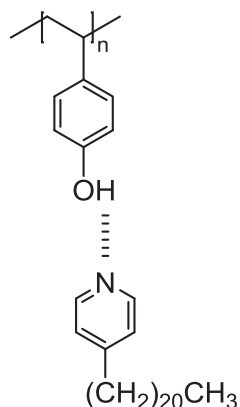
Scheme 1. Schematic representation of 4-heneicosylpyridine hydrogen-bonded to a poly(*p*-hydroxystyrene) homopolymer.

2. Experimental section

2.1. Materials

Iodine (I$_2$, Boom, 99.5%), triphenylphosphine (PPh$_3$, Merck, 99%), imidazole (Aldrich, 99%), sodium thiosulphate pentahydrate (Na$_2$S$_2$O$_3$ · 5H$_2$O, Merck, 99.5%), 1-hexadecanol (Sigma–Aldrich, 99%), 1-octadecanol (Acros, 95%), 1-eicosanol (Acros, 98%), dichloromethane (CH$_2$Cl$_2$, Lab-Scan, 98%), ethyl acetate (Acros, 99%), hexane (Lab-Scan, 99%), diisopropylamine (Acros, 99%), *n*-butyllithium (*n*-BuLi, Aldrich, 2.5 M solution in hexane), *sec*-butyllithium (*s*-BuLi, Aldrich, 1.4 M solution in cyclohexane), 4-picoline (Acros, 98%), ammonium chloride (NH$_4$Cl, Acros, 99%), diethyl ether (Lab-Scan, 99.5%), hydrochloric acid (HCl, Merck, 37%), 1,4-dioxane (Acros, 99+%) and acetone (Lab-Scan, 99.5%) were used as received. Tetrahydrofuran (THF, Acros, 99.9%) used in the synthesis of 4-alkylpyridine amphiphiles was reacted with *sec*-butyllithium for 30 min at −50 °C under nitrogen atmosphere during which a yellow color indicated that the solvent was dry. Tetrahydrofuran (THF, Acros, 99.9%) used in the anionic polymerization was reacted with *tert*-butyllithium for 1 h at −78 °C under dry nitrogen atmosphere during which a yellow color indicated that the solvent was suitable for anionic polymerization. It was condensed at room temperature into the polymerization flask and subjected to three freeze−pump−thaw cycles. 4-*tert*-Butoxystyrene (*t*BOS, Aldrich, 99%) was distilled twice under reduced pressure from finely ground CaH$_2$ and stored under nitrogen at −18 °C. Methanol (MeOH, Lab-Scan, 99.8%) was degassed by nitrogen gas flow for 1 h at room temperature.

2.2. General procedure for the synthesis of alkyl iodides

The synthesis of the alkyl iodides was carried out in oven-dried glassware under a nitrogen atmosphere. A colorless solution of triphenylphosphine (13.53 g, 51.6 mmol) in 380 mL of anhydrous CH$_2$Cl$_2$ was slowly added to iodine (13.17 g, 51.9 mmol) at r.t. under a nitrogen atmosphere. This mixture was stirred for approximately 15 min in which a color change was observed from colorless to dark brown. Subsequently, imidazole (7.05 g, 103.5 mmol) was added which resulted in an orange suspension containing yellow imidazole crystals. After stirring for 15 min, a solution of the appropriate alcohol (41.2 mmol) in 100 mL of anhydrous CH$_2$Cl$_2$ was added and the reaction mixture was heated at reflux temperature for 20 h. The CH$_2$Cl$_2$ was removed under reduced pressure and the residue was diluted with 450 mL ethyl acetate giving a yellow−brown solution. A solution of Na$_2$S$_2$O$_3$ · 5H$_2$O (18.00 g, 72.5 mmol) in 125 mL H$_2$O was added to reduce the remaining iodine. The now colorless organic layer was separated, washed with three portions of brine (160 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo to yield a sticky white/yellow solid. The product was extracted by stirring the solid in hexane (250 mL) for 1 h. The solids were removed by filtration and the filtrate concentrated in vacuo yielding the alkyl iodides (39.5 mmol, 96% yield) as off-white solids. All the alkyl iodides were obtained with yields above 90% and were stored at 6 °C, protected from light, until further use.

Hexadecyl iodide: (13.9 g, 96% yield) ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.88$ (t, CH$_3$), 1.1−1.5 (br m, CH$_2$), 1.82 (m, CH$_2$), 3.20 (t, CH$_2$) ppm.

Octadecyl iodide: (14.1 g, 91% yield) ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.88$ (t, CH$_3$), 1.1−1.5 (br m, CH$_2$), 1.82 (m, CH$_2$), 3.19 (t, CH$_2$) ppm.

Eicosyl iodide: (15.8 g, 94% yield) ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.88$ (t, CH$_3$), 1.1−1.5 (br m, CH$_2$), 1.82 (m, CH$_2$), 3.19 (t, CH$_2$) ppm.