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Phase equilibria in binary systems formed by a hyperbranched aliphatic polyester and alcohols

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ABSTRACT

Hyperbranched polymers (HBPs) possess unique properties that make them interesting for use in a wide variety of applications. Examples are their potential use in separation processes such as distillation and solvent extraction. The design of the separation process demands a thorough knowledge of the phase behaviour in systems composed of HBPs and common organic solvents. This contribution reports on the phase behaviour in binary systems formed by the hyperbranched polyester H3200 and alcohols. Both liquid–liquid and solid–liquid equilibria were investigated. It was shown that a small amount of water present in these systems has a significant impact on the extent of the liquid–liquid phase split. At temperatures below 325 K alcohol solutions of H3200 form gels over a wide concentration range of the polymer. It seems that in these systems gelation results from arrested phase instability.

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1. Introduction

Highly branched dendritic macromolecules with a complex architecture and a large number of surface functional groups are a relatively new class of polymers. They have properties different from those of linear polymers of the same molecular mass: lower flexibility, a significant end group effect, lower viscosity in solutions and high solubility in common solvents. The two main classes of dendritic macromolecules are random hyperbranched polymers and dendrimers. As opposed to dendrimers, random hyperbranched polymers are in fact mixtures of species differing in molecular weight and the degree of branching. Nevertheless, hyperbranched polymers have more possibilities of potential applications, since they are less expensive and simple to produce. There are still ongoing discussions as to the extent to which dendrimers and hyperbranched polymers possess similar properties [1].

The properties of hyperbranched polymers are affected by the nature of the backbone and end group functionalities, the degree of branching, the chain length between branching points, and the molecular weight distribution. Among these factors the structure of the terminal groups is the one that influences the properties of hyperbranched macromolecules most of all. Thus, by controlled functionalization of the end groups the properties of HBPs can easily be modified to tailor their properties to specialized purposes. Based on the highly branched architecture and the large number of terminal functional groups, various manners of modifying hyperbranched macromolecules have been developed, such as end-capping with short chains or organic molecules and terminal grafting via living polymerization. The nature of terminal functional groups influences, among others, the glass transition temperature and the solubility of hyperbranched polymers.

Both the liquid–liquid as well as the solid–liquid equilibria of the HBPs in solution have to be known in order to develop a process with HBPs. Overviews of phase equilibria in solutions of hyperbranched polymers have been presented by Seiler [2] and Žagar and Žigon [3]. High pressure phase equilibria for HBP + carbon dioxide + alcohol systems have also been investigated [4]. From the presented results it is clear that the understanding of the phase behavior of pure HBPs and their solutions is still at its infancy. The thermodynamic description of phase equilibria in these systems is likewise still not satisfactory [4,5]. This is not surprising since the theoretical description of hyperbranched macromolecules is still under development [1].

The most popular and commercially available hyperbranched polymers terminated with OH groups are polyether (based on glycidol–Polyglycerol®) and polyester (based on 2,2-bis(hydroxymethyl)propionic acid–Boltorn®). It is for this reason that these

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polymers and their modifications have been investigated most often. Among all the investigated HBPs the most promising properties from the technological point of view have been reported for the polyester Boltorn H3200 synthesized from Boltorn H30 through the esterification of OH-end groups with a mixture of eicosanoic and docosanoic acids [6]. In fact this polymer possesses very interesting properties. Being amphiphilic H3200 macromolecules form stable monolayers at the air/water interface and can be efficiently transferred onto a solid substrate [7]. This paper presents the results of experimental investigations of liquid–liquid and solid–liquid phase equilibria of systems containing H3200 and alcohols. The samples of the H3200 polymer used in this study were carefully characterised by NMR spectroscopy and gas permeation chromatography (GPC). The influence of the presence of water on the phase behaviour of selected H3200 solutions is elaborated and the properties of the solid phase precipitated from alcohol solution were investigated.

2. Experimental section

2.1. Materials

Perstop AB (Sweden) produces a series of hydroxyl-functional hyperbranched polyesters based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) with an ethoxylated pentaerytriol core, designated as Boltorn H20, H30, and H40. Boltorn H3200, the hyperbranched polymer used in this work, is synthesized from Boltorn H30 through the esterification of OH-end groups with a mixture of eicosanoic and docosanoic acids leading to C20/C22 (1:3) alkane chains as end groups.

The commercially available propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, 2-methylpropan-2-ol, pentan-1-ol, hexan-1-ol, 6-methylheptan-1-ol, hexane, butan-1,4-diol, hexan-1,2-diol, heptan-1,7-diol were purchased from Aldrich Chem. Co. In the first experiments all the solvents were used without further purification. Next, the solvents were dried over molecular sieves. The water content in fresh and dried solvents was determined by means of the Fisher method immediately before measurement.

2.2. Characterization of the H3200 polymer

The investigated polymers were characterized using Nuclear Magnetic Resonance (NMR) spectroscopy. For all the samples ^{1}H and ^{13}C spectra were recorded on a Bruker DRX Avance 300 MHz. The spectra of the polymers were measured in CD_2Cl_2 and DMSO-d6 solutions at 298 K. All the polymer solutions were prepared in the same way. An appropriate amount of the polymer was placed in a 5 mm NMR tube which was connected to the vacuum line through a ball joint. The tube with the polymer was kept at high vacuum at 343 K for about 24 h to remove any traces of water. The dry solvent was vacuum transported to the NMR tube. Then the tube was sealed. The concentration of the solution was established by weight.

Gel permeation chromatography (GPC) measurements were performed on an Agilent chromatographic setup coupled with two detectors: a Knauer Refractive Index Detector and a Wyatt Technology DAWN multi-angle laser light scattering (MALLS). A Polymer Laboratories PLGel 5 μm MIXED-C column with a length of 300 mm and inner diameter of 7.5 mm was used. Dichloromethane served as the mobile phase with a flow rate of 0.80 ml/min. The measurements were performed at a temperature of 303 K.

2.3. Phase equilibria measurements

Apparatus for measurement of cloud points in polymer solutions as a function of temperature, pressure, and concentration was used. The construction of the equipment is based on a design originally proposed by Szydlowski et al. [8]. Since significant modifications were made in comparison to the original apparatus a brief description of the equipment is given. A schematic diagram of the device is presented in Fig. 1. The heart of the device is a thick walled glass capillary **A** clamped with a clamp of variable length **B**. The top Swagelock type cap is connected with a Valco four way chromatographic valve **C** through a stainless steel capillary with 0.05 mm inside diameter. The valve together with two precise HAMILTON syringes **F** made accurate dosing of the solvent into the glass capillary possible. At the bottom there is a stainless steel capillary **D** attached to a pressure transducer **E** filled with mercury as the compressing fluid. Pressure was generated by the HPLC pump filled with methanol and measured by a pressure transducer (CAREX, Poland) with a resolution of 0.01 MPa. The transducer was calibrated against the dead weight pressure gauge. The capillary system was connected to a liquid chromatography pomp enabling stabilization of the pressure to within ±0.02 MPa. The part of the equipment within the dashed line as shown in Fig. 1 was immersed in a water thermostat enabling stabilization of the temperature to within ±0.01 K. The temperature was measured by a platinum resistance probe, which had been calibrated against a legalized thermometer (SYSTEMTEKNIK, Sweden, Model S2541). The thermostat was equipped with a glass window, which made the observation of the capillary and the sample trough optical system possible. The sample in the capillary was stirred by a small magnet **G** covered with glass driven by an external strong magnet. The volumes of the investigated samples varied from 0.2 to 2 cm^3.

Before loading of the capillary the stirring bar was immersed in mercury. A solid polymer sample was dosed into the capillary. The polymer sample was placed on the mercury surface. The amount of the polymer was determined by weight. Then the mercury was raised to the top of the glass capillary to minimize the volume of the trapped air and the capillary was closed and clamped. After immersion of the capillary in the thermostat, an appropriate amount of the solvent was added from a 100 μL syringe with a resolution of

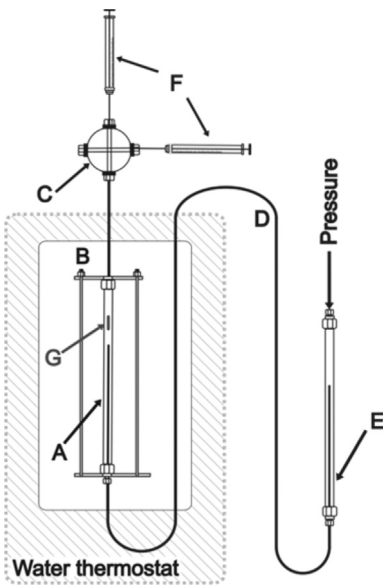

Fig. 1. Schematic diagram of apparatus for measurement of cloud points.

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