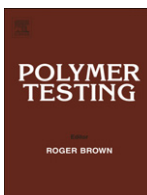




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Material behaviour

Entanglement and phase separation in hyperbranched polymer/linear polymer/solvent ternary blends

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ABSTRACT

Hyperbranched polyethylene (HBPE)/linear polystyrene (PS)/chloroform (CF) solution was selected as a model system to investigate the effect of branching structure on entanglement and phase separation behavior in semi-dilute ternary polymer solutions. All the HBPE materials in this work were found to have similar chain architectures and the critical molecular weight was estimated to be 81.2 kDa. The results obtained by elastic light scattering and intrinsic fluorescence methods suggested that all ternary solutions exhibited UCST transition behavior upon cooling. Also, it was found that the increase in the molecular weight of PS led to increase in the phase separation rate, consistent with de Gennes prediction. However, the increase of molecular weight of HBPE did not monotonously reduce the compatibility of polymer components and the phase separation rate in ternary blends is as follows: medium molecular weight HBPE (HBPE-M) > high molecular weight HBPE (HBPE-H) > low molecular weight HBPE (HBPE-L). This abnormal behavior can be explained by the fact that, (i) for HBPE-L, no entanglements between HBPE chains occurred and the branching effect can be ignored, and (ii) for HBPE-M and HBPE-H, entanglement of HBPE chains can be formed, and the dilution of branches on entanglement of backbones should be taken into consideration, that is, the shorter the branches of HBPE, the higher the possibility of interpenetration of HBPE backbones between neighboring molecules and, consequently, the faster aggregation of HBPE during phase separation. Furthermore, a simple model based on decomposition reaction was proposed to quantitatively describe the phase separation kinetics and the apparent activation energies of phase separation were calculated to be -150.3 and -52.3 kJ/mol for HBPE-M/PS/CF and HBPE-H/PS/CF systems, respectively.

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1. Introduction

Phase separation in polymer blends and solutions is of great technological and theoretical interest and, consequently, has received widespread attention. de Gennes [1] claims, for two incompatible polymer species in a common good solvent, when concentration is below the dilute/semi-dilute threshold C^* ($C < C^*$), the chain connectivity will cause individual chains to be separated, swollen coils that do not

interpenetrate and thus no phase separation occurs. On the other hand, in the semi-dilute regime ($C > C^*$), each chain can be viewed as a succession of “blobs”, where each blob contains several monomers. In a good solvent, a blob does not contain monomers of other chains due to the excluded volume interactions. This reduces the number of contacts between monomers of different species and, consequently, lowers the critical temperature compared to the Flory-Huggins (FH) prediction [2,3]. To further discuss the mobility of these two incompatible polymer species in dilute and semi-dilute solutions, the intermolecular interaction of polymers is usually divided into two parts: the entanglement interaction (short-range) and hydrodynamic interaction (long-range) [4–6]. It is known that the effects of both entanglement and hydrodynamic interactions on the polymer dynamics depend on the macromolecular architecture (e.g. linear, star, branched) [7–10].

It should be noted, however, that the vast majority of experimental and theoretical studies of homopolymer mixtures have been directed at linear macromolecules, and thus the discussion is limited to this type of mixture and other architectures have hardly been mentioned. Unlike the linear polymeric systems, alternate topologies such as hyperbranched polymers provide a larger number of structural variables to affect their intermolecular interactions [11,12]. For example, hyperbranched polyesters (Boltron-40) containing poly(*N*-isopropyl acrylamide) (PNIPAM) segments with double thermoresponsive coronas exhibited an interesting two-step chain collapse and double phase transitions [13,14]. The phase transition properties of hyperbranched polyethylenimines bearing terminal IBAM units were compared with those of analogous dendrimers and it was found that the lower critical solution temperature (LCST) of hyperbranched polymers were much more sensitive to the molecular weight alteration than their dendrimer analogues [15]. Investigations of poly(ethylene glycol) (PEG)-modified hyperbranched polyethers revealed the existence of LCST and the effect of variation of the hydrophobicity in backbone-responsive hyperbranched polyethers on their LCSTs [16]. Due to the complex architectures of hyperbranched polymers, the underlying mechanism of phase separation behavior still deserves further experimental and theoretical study.

Since the topology of polyethylene varying from linear with moderate branching to hyperbranched structures can be well controlled by ethylene coordination polymerization using Pd-diimine catalysts [17], it is convenient for us to obtain polyethylene with various branching architectures. In this work, hyperbranched polyethylene (HBPE)/linear polystyrene (PS)/chloroform (CF) solution was selected as a model system to investigate the effect of branches (including branching density and molecular weight) on the entanglement in ternary polymer solutions. Furthermore, a simple model based on decomposition reaction was employed to quantitatively describe the phase separation behavior of HBPE with different molecular weights. In our previous work [18–21], both elastic light scattering (ELS) and intrinsic fluorescence spectra were found to be very simple and sensitive means to characterize the transition of molecular conformation and aggregation of macromolecular chains. Thus, herein, it was hoped that this work would

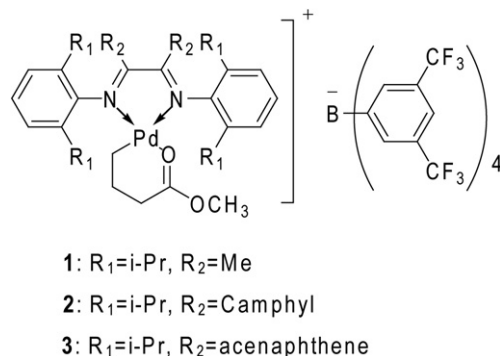
provide more valuable and fundamental information to further understand the phase transition of hyperbranched polymer in solution by applying the combination of ELS and fluorescence.

2. Experimental section

2.1. Materials and sample preparation

The Pd-diimine catalysts used in our ethylene polymerization, shown in Scheme 1, were synthesized in our laboratory according to the literature [22–24]. Ethylene polymerization was performed in a Parr pressure reactor equipped with mechanical stirring and temperature control. A typical polymerization procedure is described as follows: After thermal equilibration (35 °C) for 10 min, 0.03 mmol of Pd-diimine catalyst dissolved in 100 mL toluene was added to the reactor and the ethylene pressure was controlled at normal pressure (1.01 atm). The polymerization was allowed to continue at 20–35 °C for 15 h and then terminated by venting the reactor, the solvent being subsequently evaporated to obtain the resultant oily polymer product. To remove catalyst residues, the polymer product was redissolved in petroleum ether and the solution was passed through a column packed with neutral alumina and silica gel until it became colorless. The polymer was finally precipitated out using methanol and was dried under vacuum. The molecular weights of the products were measured by SEC on a Waters Alliance GPC 2000 system with a multiangle laser-light scattering detector (SEC-MALS). Here, THF was used as a good solvent of HBPE, and the flow rate was 1.0 mL/min. The branching density (branches per 1000 carbon atoms) and the percentage of methyl branches in *sec*-butyl-ended branches (1B1%) were determined by quantitative ¹³C NMR spectroscopy (Varian INOVA 300M) in CDCl₃. TMS (Aldrich) was used as the internal reference. The molecular characteristics of HBPE are listed in Table 1.

Two kinds of PS with different molecular weights were used to study the effect of molecular weight of linear polymer on phase separation. PS with higher molecular weight (PS-H) ($M_n = 106.9$ kDa, $M_w = 187.6$ kDa, PDI = 1.75) was purchased from Beijing Yanshan Chem. Co. Ltd. (Beijing, China). PS with lower molecular weight (PS-L) ($M_n = 12.8$ kDa, $M_w = 14.9$ kDa, PDI = 1.16) was kindly supplied by the



Scheme 1. Catalysts used in ethylene coordination polymerization.

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