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Synthesis and properties of semi-crystalline hyperbranched poly(ester-amide) grafted with long alkyl chains used for UV-curable powder coatings

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Abstract

A series of semi-crystalline hyperbranched poly(ester-amide)s by modifying hydroxyl end groups of hyperbranched poly(ester-amide) (HP) with IPDI-C18 and IPDI-HEA in different ratios were synthesized and characterized by FTIR, NMR and GPC. Their crystallization behaviors and thermal properties determined by X-ray diffraction (XRD) and differential scanning calorimetry (DSC) showed that the high substitution degree of hydroxyl groups of hyperbranched poly(ester-amide) (HP) with IPDI-C18 resulted in higher degree of crystallization and thus glass transition temperature (T_g) up to 43 °C. The photopolymerization kinetics investigated by photo-DSC showed that the obtained semi-crystalline hyperbranched resins have high photopolymerization rate and final unsaturation conversion, which is very promising for UV-curable powder coating applications.

Keywords: Hyperbranched poly(ester-amide); Semi-crystalline; Powder coating; UV curing

1. Introduction

With increasing environmental concerns and ongoing legislations to reduce the emission of volatile organic compounds (VOCs), ultraviolet (UV)-curable coatings in which multifunctional monomers are added as reactive diluents, have been widely used due to their pollution reduction, energy conservation, high cure speed and cost-effectiveness compared to conventional solvent borne coatings [1]. Powder coatings are considered to be another kind of environmentally friendly coatings since all components are solids in the coating formulations. The most important advantage of powder coatings over liquid coatings is that they are few volatile organic compound (VOC) and nontoxic systems without liquid unreactive or reactive diluents which can partly permeate most substrates. However, conventional powder coatings are in general based on amorphous resins, which are cured in a thermally activated process at the temperature as high as 180–200 °C and with a complete cure cycle in 15–30 min [2–4]. The high temperature and long curing time to obtain a fully crosslinked film with traditional powder coatings make a real challenge when applied to heat-sensitive materials such as wood, plastic, medium density fiberboard (MDF), and preassembled articles such as motors and gearboxes. Therefore, UV-curable powder coating systems, as combination of powder coatings with UV-curing technology are developed as one of the most promising paint application systems.

UV-curable powder coatings have some favorable properties, e.g., almost no emission of by-products, excellent weathering resistance and good mechanical properties. UV curing can be performed at lower temperature than possible by thermally activated systems. Thus, it is possible to coat heat sensitive substrates such as plastic or MDF and thus to save considerable energy [5]. Another important advantage compared with a thermally activated curing system is that the UV-curing course is strictly divided from the process of melting and leveling of the molten powder; hereby there is enough time to release the entrapped air in the film and level the powder melt while having no danger of making the film crosslink before UV irradiation, which may happened in a thermally activated curing process when the temperature procedure is not carefully mastered.

However, there is a contradiction in the control of glass transition temperature (T_g) for a powder for UV curing: a high T_g to

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ensure the stability during handling, transportation and storage; a low T_g to ensure a lower viscosity in its molten state. New resins are exploited in order to solve this contradiction. Introducing crystallizable moieties is one of creative strategies [6], in which mixing amorphous resins with crystallizable monomers is a commonly used method to obtain an ideal rheological characteristic. Nevertheless, phase separation is observed between two components: amorphous resins and crystallizable monomers.

Three-dimensional dendritic polymers, which present a large degree of functionality in a molecule, are a new family of materials that have generated intense interests over the past two decades [7–11]. Due to their highly branched molecular structures, these polymers are usually unable to crystallize [12]. However, crystallization can be induced by the attachment of long alkyl chains to dendritic polymers [13–15]. Our group has described the synthesis of semi-crystalline resins based on hyperbranched poly(ether-amide) by grafting crystalline segments at first and then end-capping with UV-curable acrylic groups [16–18]. Hult and co-workers [19] have successfully investigated the possibility for preparing semi-crystalline hyperbranched polyester used in UV-curing powder coatings.

In this paper, we described the synthesis of UV-curable semi-crystalline hyperbranched poly(ester-amide)s with long alkyl chains. The photopolymerization kinetics and crystallization behaviors of the obtained products and the thermal properties of the UV-cured films were investigated.

2. Experimental

2.1. Materials

Succinic anhydride (SA), tris-(hydroxymethyl)aminomethane (THAM), isophorone diisocyanate (IPDI) and octadecyl alcohol were purchased from the Frist Reagent Co. of Shanghai, China and used as received. 2-hydroxyethylacrylate (HEA) and *N*,*N*-dimethylacetamide (DMAc) were used after drying over 4-Å molecular sieves. Di-*n*-butyltindilaurate (DBTDL) as a catalyst was purchased from the Third Reagent Co., Beijing, China. Benzoyl-1-hydroxyl-cyclohexanol (Irgacure 184) as a photoinitiator was supplied by Runtec Co., China.

2.2. Synthesis

2.2.1. Hyperbranched poly(ester-amide) (HP)

The hyperbranched poly(ester-amide) with hydroxyl end groups (HP) was prepared by thermally polycondensation of succinic anhydride (SA) and tris-(hydroxymethyl) aminomethane (THAM) at the absence of catalysts and solvents, as described by a procedure in literature [20].

^{1}H NMR (D_2O): δ (ppm) = 4.10–4.62 ($C^4(C\mathbf{H_2}O)_n(CH_2OH)_{3-n}$), 3.54–4.02 ($C^4(CH_2O)n(C\mathbf{H_2}OH)_{3-n}$), 2.42–2.94 (group, $OOCC\mathbf{H_2}C\mathbf{H_2}CONH$).

2.2.2. Semi-crystalline hyperbranched poly(ester-amide)

22.2 g IPDI (0.10 mol), 0.10 g DBTDL and 40 ml of DMAc were poured into a dry glass reactor which was purged with nitrogen before use to eliminate moisture. 0.10 mol HEA (or octadecyl alcohol) in 110 ml DMAc was slowly dropped into the reactor under stirring at 0 °C. After the completion of addition, the reaction was maintained for 8 h at 25 °C. Then the reactants was heated to 50 °C, and stirred until the IR absorption of hydroxyl group of HEA (or octadecyl alcohol) disappeared. The obtained half-adducts are denominated as IPDI-HEA (or IPDI-C18).

A given amount of IPDI-C18 dissolved in DMAc was added dropwise into the HP solution of DMAc in different molar ratios of IPDI-C18/HP and then stirred continuously at 50 °C until the IR absorption peak at 2250 cm^{-1} for NCO group disappeared. The calculated amount of IPDI-HEA was dropped into the above reactant and reacted at 50 °C until the peak for NCO group completely disappeared. The reaction mixture was then individually precipitated into distilled water, then filtered and washed with acetone, and finally dried under a vacuum system giving the product as a white powder. The products were designated, using the following abbreviation: HP-L_xD_y, where x and y represent the substitution degree of IPDI-C18 (long alkyl chain: L) and IPDI-HEA (acrylic double bond: D), respectively. For example, HP-$L_{50}D_{25}$ describes a powder resin based on hyperbranched poly(ester-amide) (HP) theoretically end-capping with 50% IPDI-C18 and 25% IPDI-HEA among the total number of hydroxyl group of HP.

^{1}H NMR ($CDCl_3$): δ (ppm) = 5.8–6.5 ($C\mathbf{H}{=}C\mathbf{H_2}$), 3.6–4.64 ($C^4C\mathbf{H_2}OCO$ and $CH_2C\mathbf{H_2}OCO$), 2.32–3.10 (group, $OOCC\mathbf{H_2}C\mathbf{H_2}CONH$), 0.6–2.01 (other hydrogens in long chains and cyclohexane).

2.3. UV curing

The HP-L_xD_y resin with benzoyl-1-hydroxyl-cyclohexanol (Irgacure 184) (4 wt%) addition was melted at 125 °C, then applied on a glass plate with an applicator of 100 μm^{-1} gap, and exposed to a UV lamp (Hg, 1 kW, 80 W cm^{-1}, made by Lantian Co., China) to obtain a cured film.

2.4. Measurements

The FTIR spectra were obtained with a Fourier transform IR spectrophotometer MAGNA-IR 750 (Nicolet Instrument Co., USA) by averaging 32 scans at a resolution of 2 cm^{-1}.

The nuclear magnetic resonance (NMR) spectra were recorded with a DMX-500 (Bruker Co., Zurich, Switzerland) instrument using $CDCl_3$ or D_2O as a solvent and with the residual ^{1}H solvent peak as reference.

The gel permeation chromatography (GPC) analysis was performed with a Waters 1525 equipment fitted with two columns (Styragel HT3 and HT4 THF 7.8 mm × 300 mm column) connected in series and a 2414 refractive index detector with THF as mobile phase.

The differential scanning calorimetry (DSC) analysis was performed on a PERKIN ELMER pyris 1 DSC insrument, calibrated according to the standard procedure. The samples were heated from 0 to 200 °C at a rate of 20 °C min^{-1}.