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Fluorinated modification of hyperbranched polyesters used for improving the surface property of UV curing coatings

Hui Miao, Fenfen Bao, Liangliang Cheng, Wenfang Shi *

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Jinzhai Road 96, Hefei, Anhui 230026, PR China

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The commercial hyperbranched aliphatic polyols (H*n*) were modified by thioglycolic acid (TA) and hexafluorobutyl acrylate (HFBA) or dodecafluoroheptyl methacrylate (DFHMA) to prepare a series of fluorinated hyperbranched polyesters. For comparison, a linear fluorinated polymer, poly(*n*-BMA-co-DFHMA), was synthesized through the copolymerization of *n*-butyl methacrylate (BMA) and DFHMA. The molecular structures were characterized by ^{1}H NMR spectroscopic analysis. The synthesized polymers were incorporated into UV-curable formulations as additives, and exposed to a UV lamp. After UV curing, the wettability of the films was investigated by contact angle measurement with water and 1-bromonaphthalene. The results showed that both the hydrophobicity and oleophobicity were greatly enhanced. Moreover, the fluorinated hyperbranched polymers possessed better water and oil repellency than the copolymer poly(*n*-BMA-co-DFHMA) at a very low concentration. The surface F/C ratio values of the cured films were detected by XPS analysis, and the film with TAH20–DFHMA showed the highest F/C ratio value, indicating its most efficient aggregation effect at the film surface.

1. Introduction

Over past two decades, hyperbranched polymers have received much attention because of their unique chemical structures with a large number of terminal groups which are easily functionalized according to requirements [1,2]. Therefore, many novel hyperbranched polymers have been synthesized for various applications [3–6].

Fluorinated materials are attractive recently because of their unique properties, such as extremely low energy surface, and thus excellent water and oil repellency, solvent resistance, and acid and alkali stability [7–10]. Therefore, the fluorinated materials are considered to be used for high performance coatings on different substrates, showing the good protection against corrosion, weathering, and environmental pollution [11–14].

The fluorinated hyperbranched polymers combine the advantages of both fluorinated and highly branched polymers [15–17]. The fluorinated hyperbranched polyimides were prepared and used for optical wave guide materials, showing good thermal stability and low optical absorption in the near infrared region [18]. Sangermano et al. reported that the fluorinated aromatic–aliphatic hyperbranched polyesters used as additives in cationic photopolymerization systems protected the cured coatings from aggressive solvents, enhanced the film hardness, and allowed a low energy surface [19]. In our previous work, the fluorinated hyperbranched polyester acrylates were applied into UV curing formulations, showing that the cured films possessed low surface energy and good water and oil repellence [20].

In this work, a series of hyperbranched polyesters with different numbers of fluorinated groups at the terminals, such as TAH*n*–HFBA and TAH*n*–DFHMA, and a linear fluorinated copolymer poly(*n*-BMA-co-DFHMA) for comparison were synthesized based on thioglycolic acid modified Boltorn^{TM} products (TAH*n*) and characterized by ^{1}H NMR spectroscopy. The synthesized fluorinated polymers were blended into the UV curable formulations as additives. After curing, the contact angle measurement was carried out for the films using water and 1-bromonaphthalene as test liquids. The results showed that the synthesized hyperbranched polymers enhanced the hydrophobicity and oleophobicity of the UV cured films. Moreover, the F/C ratio value of the UV cured film surface was detected by XPS analysis, and showed that the film with TAH20–DFHMA addition has the highest F/C value, indicating that TAH20–DFHMA has the most efficient aggregation effect at the film surface.

2. Results and discussion

2.1. Characterization

To evaluate the surface aggregation ability of different kinds of fluorinated chemicals in UV-curable formulations, two fluorinated

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* Corresponding author. Tel.: +86 551 3606084; fax: +86 551 3606630.
E-mail address: wfshi@ustc.edu (W. Shi).

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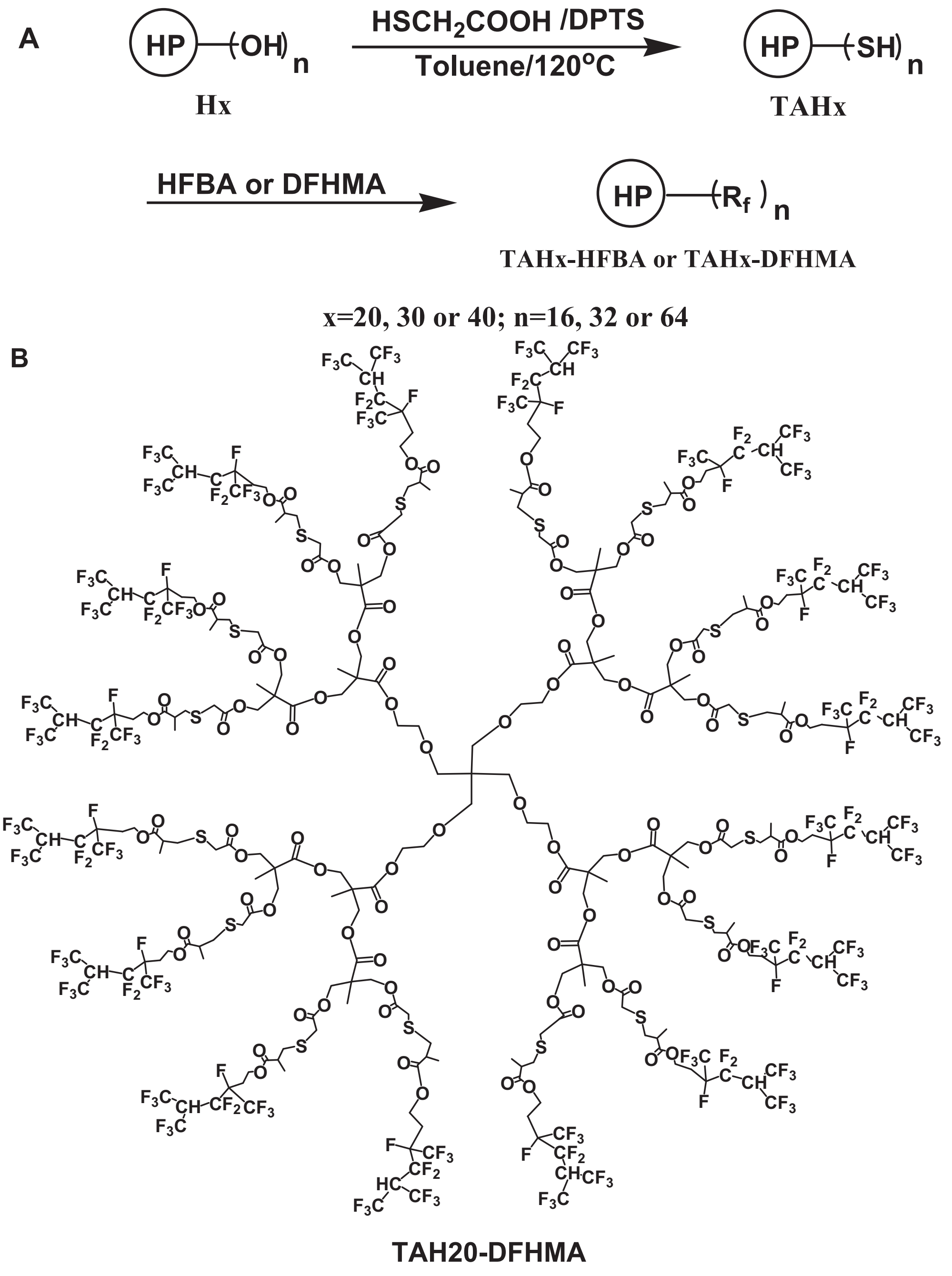

Scheme 1. Synthesis routes for fluorinated hyperbranched polymers (A) and ideal schematic representation of TAH20–DFHMA (B). (HP: Boltorn H polymer, DPTS: 4-dimethylaminopyridine p-toluenesulfonate).

monomers, hexafluorobutyl acrylate (HFBA) and dodecafluoroheptyl methacrylate (DFHMA), were used to modify the hyperbranched polyester. The synthesis route and the ideal structure of TAH20–DFHMA are shown in Scheme 1A and B, respectively. A linear copolymer, poly(*n*-BMA-co-DFHMA), was also synthesized for comparison (Scheme 2).

Boltorn^{TM} H20, H30 and H40 are a series of hyperbranched polyester and theoretically have 16, 32, and 64 terminal hydroxyl groups. The hydroxyl groups were functionalized by esterification with thioglycolic acid (TA) as shown in Scheme 1A. In the ^{1}H NMR spectrum of TAH20 in $CDCl_3$ (Fig. 1), the signals at the chemical shifts of 2.03–2.06 ppm were assigned to the thiol proton, while that at 4.29–4.39 ppm were assigned to the methylene protons of original hydroxylmethyl group in 2,2-bis(hydroxymethyl) propionate (BMPA, the structural unit of H20), which had shifted to the high δ value after esterification. According to the integration results from the NMR peaks, the thiol group number was less than the theoretically calculated value, compared with the integral value of signal peak for the methylene protons of $-CH_2-SH$ at 3.28–3.31 ppm, which was possibly because of the integral inaccuracy of active hydrogen of the thiol proton in the NMR analysis. Moreover, the signals of methylene protons of disulfides ($-CH_2-S-S-CH_2-$) at the higher chemical shifts were not observed, indicating that no apparent oxidation happened for the thiol groups. The ^{1}H NMR spectra of TAH30 and TAH40 were also shown in Fig. 1, showing the similar curves as TAH20. From the integral result, the conversion of hydroxyl group of H20 was calculated to be 98%, indicating that almost all hydroxyl groups were esterified by