

STUDY ON UV CURABLE POWDER COATINGS BASED ON HYPERBRANCHED POLYMERS*

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Abstract By introducing semicrystalline moieties into hyperbranched molecular structures three kinds of prepolymers of potential use as UV powder coatings were prepared and characterized.

Keywords Hyperbranched polymer, Crystallinity, UV powder coating

INTRODUCTION

UV-curable powder coatings have proved attractive in recent years due to many advantages. They are environment-friendly (no VOC), economically attractive and have many other excellent qualities^[1]. However, one of the main advantages is that the UV powder coatings can be cured at lower temperature, which makes them ideal for coating heat-sensitive materials, such as wood, plastics, medium density fiberboard (MDF), and pre-assembled articles, such as motors and gearboxes^[2]. Heat-sensitive substrates demand lower cure temperature to avoid significant substrate degradation and/or deformation. Moreover, UV powder coatings need much less thermal energy just sufficient for their melting and flowing to form a continuous and smooth film over the substrate. The melting and the UV curing processes are performed separately, and no curing occurs on leveling since the powders are completely inert until irradiated with UV, which may give the final products an improved surface appearance. However, high reactivity under UV irradiation is required for an efficient powder coating system. A thermally stable photoinitiator which initiates fast curing under UV irradiation when the coating melts at 110°C~120°C can meet the requirement^[3, 4]. To ensure the high chemical stability during handling, transportation, and storage, a higher glass transition temperature (T_g) of the powder is required. In order to obtain good spreading of the molten film over the substrate, the viscosity of the prepolymer in the molten state should be sufficiently low. It has been found that introducing a crystallizable moiety into the prepolymeric structure may obviously reduce the viscosity in the molten state. This means that the viscosity decrease of a crystalline polymer during melting is usually larger than that of amorphous polymers with comparable molecular weight heated over T_g . In addition, crystalline polymers may provide coatings with better mechanical properties, in particular excellent flexibility^[5].

Dendritic hyperbranched polymers have been of particular interest during the last 10 years. These materials present a non-interchain entangling architecture which may provide poor crystallinity, but a large degree of functionality which gives extraordinary possibilities for tailoring a polymer for a certain application by chemical modification of the end-groups. Moreover, the nature of the terminal groups has also been found to affect the

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properties of the products. Therefore, it is possible to prepare molecules with amorphous interior and (semi)crystalline long chains as well as (meth)acrylates at the terminals. According to previous work by end-capping the hyperbranched polymers with (meth)acrylate groups, hyperbranched resins suitable for UV-curable coating applications were obtained^[6, 7]. However, little work has been performed on the preparation of low temperature UV-powder coatings with hyperbranched polymers. Hult and his coworkers have successfully grafted ϵ -caprolactone onto the hydroxy-functional aliphatic hyperbranched polyester, and then end-capping of the polycaprolactone chains with methacrylate groups, which were UV cured in the molten state to yield flexible films^[8].

In this article, the crystallinity of hyperbranched prepolymers based on different monomers and core molecules modified with octadecyl isocyanate and acryloyl chloride, which may be used for UV powder coatings, was investigated with X-ray diffraction spectra and DSC measurements.

RESULTS AND DISCUSSION

Hyperbranched Aliphatic Polyesters (Boltorn™-H20)

The hyperbranched polyester, Boltorn™-H20 with hydroxyl-functional terminals is one of the commercial product series produced by Perstorp AB, Perstorp, Sweden, which is the second generation of hyperbranched polyesters based on 2,2-bis(methylol) propionic acid (bis-MPA) as an AB₂ monomer and polyol as a core molecule with a theoretical molecular weight of 1750 g mol⁻¹ and an average of 16 hydroxyl end groups per molecule. As mentioned above, the synthesized (semi) crystalline powder coatings based on Boltorn™-H20 have polycaprolactone segments and methacrylate end-groups. It was found that the melting points (T_m) of the final products varied with the length of polycaprolactone chain in the range of 36°C~50°C^[8]. In this study the different molar ratios of acryloyl chloride to octadecyl isocyanate (0, 1/4, 2/3, and 3/2) were used to modify the hydroxyl-functional groups of Boltorn™-H20 in obtaining (semi) crystalline UV curable powder coatings. The schematic outline of the modification is shown in Fig. 1.

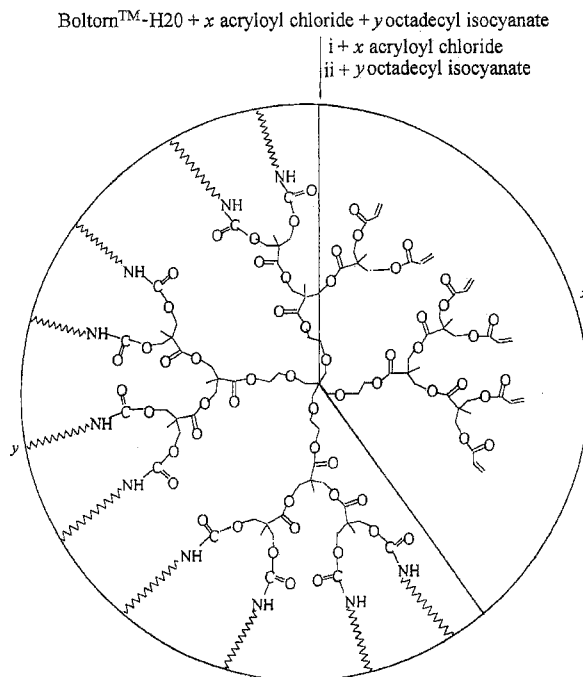


Fig. 1 A schematic outline of the modification of Boltorn™-H20 with acryloyl chloride and octadecyl isocyanate

The differential scanning calorimetry (DSC) spectra and the data obtained before and after modification of BoltornTM-H20 are presented in Fig. 2 and Table 1, respectively. H20-xA means a modification of $x\%$ hydroxyl groups of the molecule with acryloyl chloride and the residuals with octadecyl isocyanate. It can be seen from Fig. 2 that two endothermic peaks appeared in the DSC spectra after modification by addition of octadecyl isocyanate moiety in each case. This means there are two crystalline regions with different melting points (T_{m1} and T_{m2}) for each powder samples. It was also found that the variation of the ratio of acryloyl chloride to octadecyl isocyanate causes small changes of the two T_m s in the range of $56^\circ\text{C}\sim 48^\circ\text{C}$ and $105^\circ\text{C}\sim 111^\circ\text{C}$, respectively. However, it is very clear that the melting point T_{m1} is slightly lowered on addition of the acryloyl chloride, and the degree of crystallinity of the products with larger weight fraction of the crystalline moieties is higher. However, end-capping of a certain amount of acrylate groups in the molecule is very necessary, and may result in higher crosslinking density on UV irradiation and thus in the improvement of the mechanical properties of the final product.

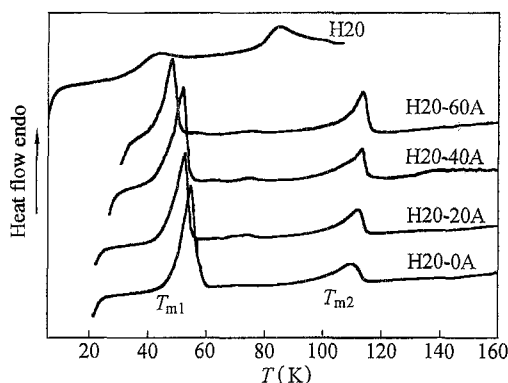


Fig. 2 DSC spectra of BoltornTM-H20 before and after modification with octadecyl isocyanate and acryloyl chloride

Table 1. The T_m of BoltornTM-H20 before and after modification

Polymer	Percent of modifier (%)		Theoretical molecular weight	Density of double bond (mmol/g)	T_{m1} ($^\circ\text{C}$)	T_{m2} ($^\circ\text{C}$)
	Acryloyl chloride	Octadecyl isocyanate				
H-20	0	0	1747		80	
H20-0A	0	100	6475		56	105
H20-20A	20	80	5714	0.56	53	109
H20-40A	40	60	4923	1.31	52	111
H20-60A	60	40	4156	2.31	48	111

Hyperbranched Aliphatic Poly(amide-ester)s (HAPAE)

In order to raise the T_m of a resin and the thermal stability of a cured film, amide bonds were introduced in the hyperbranched molecules. The HAPAE were synthesized based on 4-*N,N*-di(2-hydroxy ethyl)-4-ketobutyric acid as an AB₂ monomer (repeating unit) prepared by the reaction of succinic anhydride and diethanol amine, and 2-ethyl-2-(hydroxy methyl)-1,3-propanediol as a core molecule. The resulting polymer with hydroxyl terminal groups was modified with acryloyl chloride to get the UV curable HAPAE, and the idealized formula is shown in Fig. 3. This prepolymer exhibits high thermal stability after curing (Fig. 4). After modifying 60% of the hydroxyl groups at the chain terminals with octadecyl isocyanate and the residuals with acryloyl chloride, the resin became a crystalline white powder. The DSC spectrum is shown in Fig. 5. As has been shown, the prepolymer also has two T_m s, i.e. 53°C and 109°C , which is the same result as that for the BoltornTM-H20 system described in the previous section.

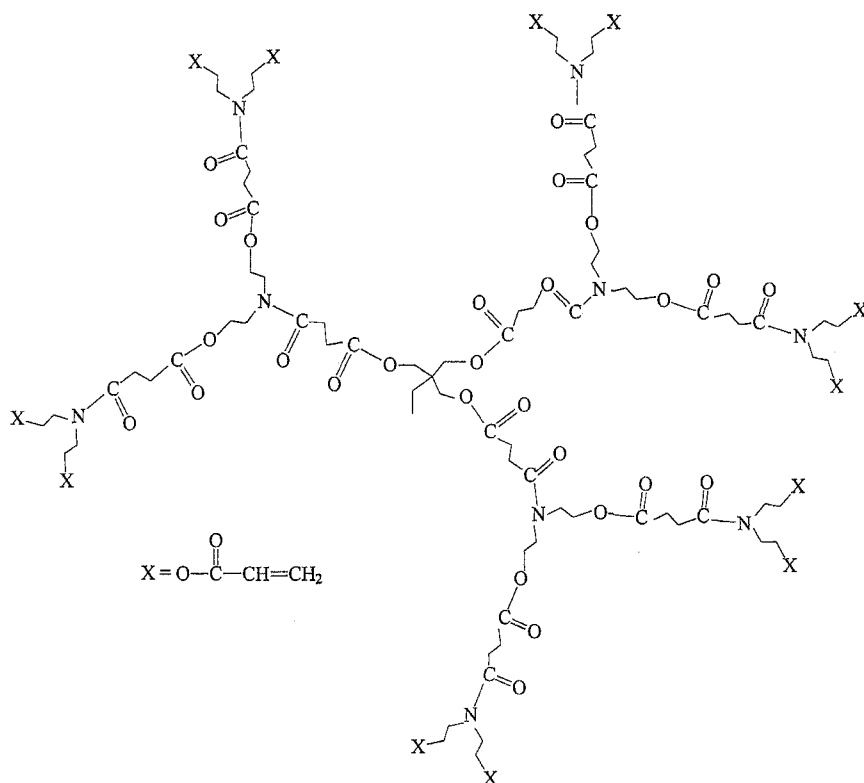


Fig. 3 Idealized formula of the HAPAE (2nd generation)

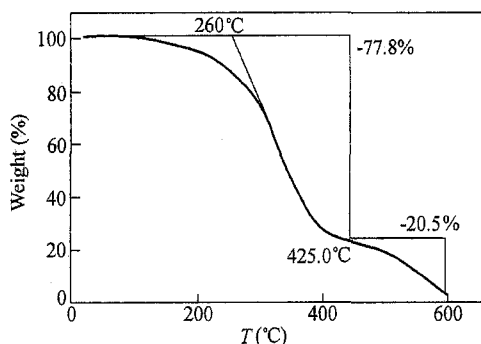


Fig. 4 Thermogravimetric analysis as HAPAE-2 at a heating rate of 10 K/min

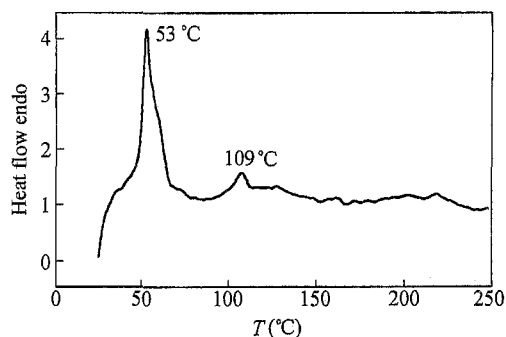


Fig. 5 DSC spectrum of HAPAE modified with 60% of octadecyl isocyanate and 40% of acryloyl chloride at the ends

Hyperbranched Poly(ether-amide) (DPEA)

It is well known that introducing an ether bond into the molecular structure instead of an ester bond may give a resin of higher T_g and T_m . The DPEA was started by the reaction of hydroxyl groups of polyol with acrylonitrile, then further reacted with alcohol in acid conditions. The obtained multi-ether compound was then further reacted with tris(hydroxymethyl)aminomethane, forming a star-shaped hyperbranched poly(ether-amide) with 4 amide and 4 ether bonds in the chains and 12 hydroxyl groups at the ends, which can be modified with glycidyl methacrylate/acryloyl chloride to form a UV/EB curable prepolymer shown in Fig. 6.

The hydroxy-functional DPEA is amorphous at room temperature as a glassy, slightly yellow solid. When using octadecyl isocyanate or myristoyl chloride to modify the hydroxyl end groups at the outer layer of DPEA partly or completely, a white powder was formed at room temperature. The introduction of the long alkyl chains

into the molecular structure can lead to the crystallization of the samples, which can be demonstrated by X-ray diffraction as shown in Fig. 7.

On modifying all and 35% of hydroxyl groups at the molecular terminals with octadecyl isocyanate a large endothermic peak appeared at 116°C and 117°C, respectively, and a T_g around 48°C for both cases also can be seen from DSC spectra, as shown in Fig. 8. By modifying 20% of the hydroxyl groups with glycidyl methacrylate, 35% with acryloyl chloride and the residuals with octadecyl isocyanate, a product with T_m of 115°C was also obtained (Fig. 9). These properties may meet the UV powder coating requirements.

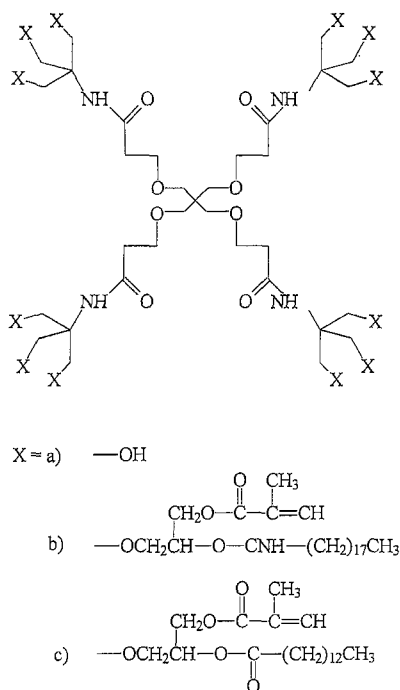


Fig. 6 Idealized formulae of DPEAs before and after modification

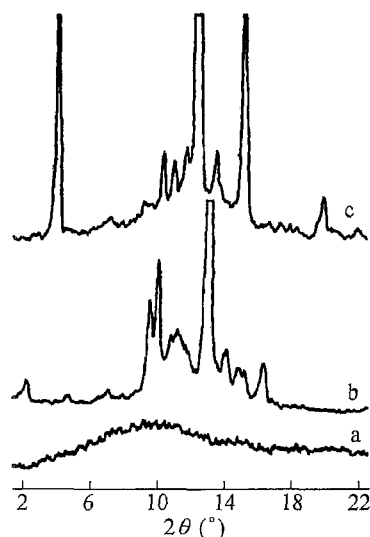


Fig. 7 X-ray diffraction spectra of DPEA before (a) and after modification with octadecyl isocyanate (b) and myristoyl chloride (c)

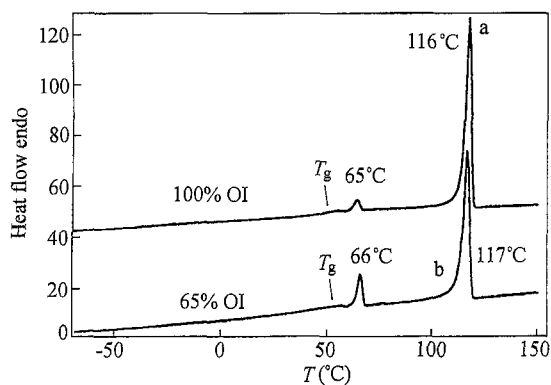


Fig. 8 DSC spectra of DPAE with all (a) and 65% (b) of hydroxyl groups modified by octadecyl isocyanate

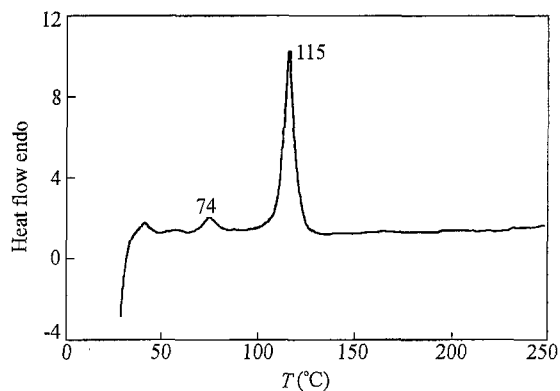


Fig. 9 DSC spectrum of DPAE-20MA-35A modified with octadecyl isocyanate and acryloyl chloride

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