Novel Concept for Low Temperature Curing Powder Coatings Based on Hyperbranched Polyesters

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The concept of using hyperbranched polymers as scaffolds for solid thermoset resin applications is de-scribed. A series of semi-crystalline methacrylate-functional aliphatic poly-esters has been synthesized and characterized for applications as solid thermoset resins, e.g., powder coating resins. The polyester resins have been crosslinked by UV irradiation producing either amorphous or semi-crystalline crosslinked films depending on the initial structure. The resins are based on hyperbranched aliphatic polyesters onto which crystalline linear aliphatic polyester chains have been grafted and end-capped with meth-acrylate moieties. The resins exhibit a rheological behavior suitable for low temperature curing powder coatings, i.e., films that can be readily formed and UV cured at temperatures below 80°C.

INTRODUCTION

Solid thermoset resins have increasing importance in several fields, especially in powder coatings. Powder coatings are based on resins that are solid at ambient temperature and flow at elevated temperature to form a uniform coating layer. Most systems are based on amorphous reactive polymers that crosslink in the molten state forming a thermoset coating. Thermoplastic powder coatings also exist.[1]

One of the main advantages of powder coatings is that they are zero-VOC systems (i.e., they contain no solvents), which is advantageous from both environmental and economical aspects. Until now, the use of powder coatings mainly has been directed towards the coating of metal substrates, since the high curing temperatures limit their use on heat sensitive substrates such as wood and plastics. The lowest curing temperature at this point is around 120°C for the conventional systems on the market. This limit is set by the combination of two factors, storage stability and the film fusion process. A powder coating must be storable at 30°C without fusing together, which is why the glass transition temperature (T_g) of the polymer must be 60°C or higher. The powder must melt and form a homogeneous film, a process that requires a fusion temperature at least 50°C above T_g. This reasoning is valid for amorphous polymers and results in a minimum curing temperature of about 110°C.[2]

The desire to apply powder coatings on heat-sensitive substrates has triggered extensive research during the last decade, and several solutions have been proposed. One way to reduce the melt viscosity is to introduce crystallinity into the polymer system,[3-5] since the viscosity decreases more rapidly above the melting transition compared to the decrease in viscosity above T_g for an amorphous polymer. This allows film formation at lower temperatures while still retaining good storage stability at room temperature. The fast decrease in viscosity may, however, cause sagging problems. The low viscosity may also cause unwanted penetration into the substrate if it is porous, e.g., wood, and the molar mass of the crystalline component is too low. Non-crystallized low molecular weight components also tend to act as softeners for the system. Hence, the optimum rheological performance is a rapid drop in viscosity above the melting point but only down to a specified level.

A low curing temperature also requires an initiating system that is activated at low temperatures but is stable at room temperature. This is difficult to achieve with conventional thermal initiators, which is why UV initiation has been suggested.[4,6] Thermally stable UV initiators will ensure chemical stability at ambient temperatures, and the crystalline component will induce

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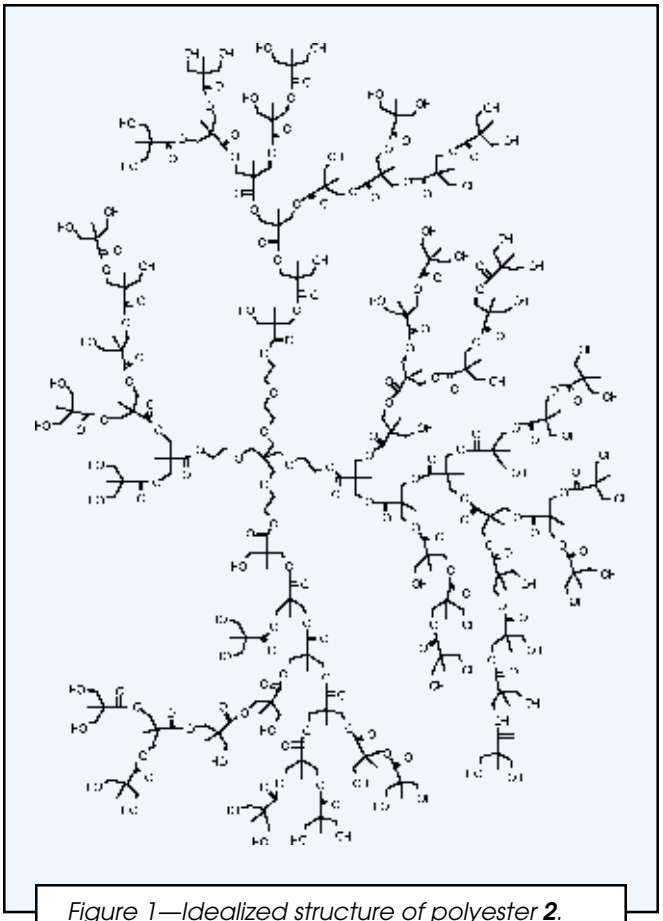

*Figure 1—Idealized structure of polyester **2**.*

good flow properties above the melting point. The processes to obtain stable powder particles and subsequent electrostatic deposition of these to a substrate will add further demands on the rheological/physical properties on the resins. The present study does not present data addressing these demands, but focuses merely on the basic rheological properties of these materials.

Another research area in the field of macromolecules is related to the improvement of material properties by changing the macromolecular architecture.[7] One group of these materials which has obtained increasing attention

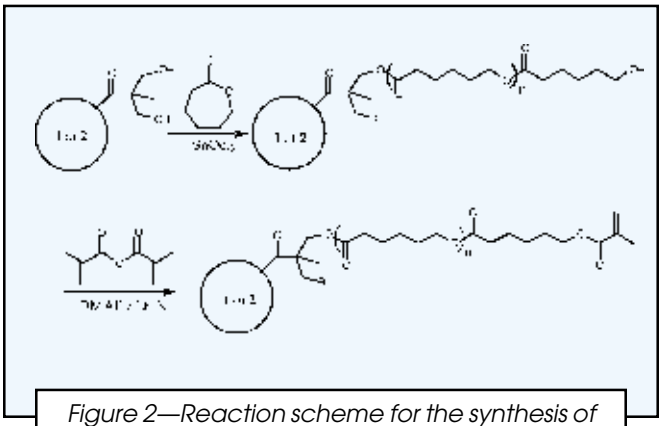

Figure 2—Reaction scheme for the synthesis of the methacrylate functional semi-crystalline polyesters.

in recent years is dendritic polymers,[8] comprising dendrimers and hyperbranched polymers. Dendritic polymers are highly branched macromolecules based on AB_x-monomers, introducing a potential branch point in every repeat unit. Dendritic polymers have been demonstrated to possess unique properties, such as low melt viscosity as a function of molar mass and high solubility in various solvents compared to their linear analogs.[9] It has been demonstrated that hyperbranched polymers can act as scaffolds for functional groups (polymer structures)[10] and that crystallinity can be introduced by the attachment of crystallizable end-groups onto the polymers.[11] The grafting of crystallizable chains to a hyperbranched polymer, resulting in intermediates between star- and hyperbranched polymers, has also been demonstrated.[12]

This paper describes the synthesis of solid semi-crystalline resins based on hyperbranched polymers onto which crystalline segments are grafted and end-capped with crosslinkable methacrylate groups. The chemical, rheological, and final network properties of these polymers are described. It is demonstrated how these properties fulfil some of the demands for low temperature curing powder coatings.

EXPERIMENTAL

Materials

Two different hydroxyl-functional hyperbranched aliphatic polyesters were supplied by Perstorp AB, Perstorp, Sweden: (1) Boltorn™-H20, **1**, with a theoretical molecular weight of 1750 g mol^{-1} and an average of 16 hydroxyl end groups per molecule; and (2) Boltorn™-H40, **2**, with a theoretical molecular weight of 7300 g mol^{-1} and an average of 64 hydroxyl end groups per molecule (*Figure* 1). The hyperbranched polyesters are based on 2,2-bis(methylol) propionic acid (bis-MPA) as AB_2-monomer and ethoxylated pentaerytritol as core molecule (5EO/penta). ε-Caprolactone (ε-CL) was dried over CaH_2 and distilled twice before use. Irgacure 184™ (1-hydroxy-cyclohexyl-phenyl-ketone) was obtained from Ciba-Geigy and used as received. All other chemicals were purchased from Aldrich or Lancaster and used as received.

The following type of abbreviation has been used to describe the different polymers. P2G–ε–PCL(DP=10)-MA where P2G indicates that a second generation hyperbranched polyester (Boltorn-H20) has been used as starting material; ε–PCL(DP=10) indicates that ε–polycaprolactone chains with a degree of polymerization of 10 have been attached to the polyester; and MA indicates that the PCL chains are end-capped with methacrylate groups.

Equipment

^{1}H-NMR and ^{13}C-NMR were recorded on a Bruker AM 400, at 400 and 100 MHz, respectively, using $CDCl_3$ as solvent. The solvent signal was used as internal standard. Size exclusion chromatography (SEC) was

performed on a Waters SEC system using a solvent delivery system (Model 510), automatic injector (WISP 710B), and a differential refractometer (Waters 410) as a detector, and three PLgel 10 µm mixed-B columns from Polymer Labs. THF, 1.0 ml min^{-1}, was used as the mobile phase. Calibration was carried out using linear polystyrenes of known molecular weight and dispersity.

Table 1—Synthesized Polyesters 3-6 with Basic Data

Polyester No.	DP, ε-PCL[a]	M_n, theor.[b] (g mol^{-1})	M_n, SEC (g mol^{-1})	PD, SEC	Yield (%, w/w)
3 P2G–εPCL(DP=10)	10.0	20 000	19 700	1.16	77
4 P2G–εPCL(DP=30)	41.2	77 000	48 200	1.14	82
5 P4G–εPCL(DP=10)	10.5	84 000	34 200	1.29	92
6 P4G–εPCL(DP=30)	21.2	162 200	48 600	1.20	57

(a) DP of each PCL chain from ^{1}H-NMR.
(b) Theoretical value based on ^{1}H-NMR data.

Calorimetric studies were carried out on a Mettler Toledo DSC 820 equipped with a Mettler Toledo Sample Robot TSO801RO calibrated using standard procedures. Photo-DSC experiments were performed on a similar Mettler Toledo DSC equipped with a Hamamatsu UV Spot Light Source L5662. FTIR measurements were performed on a Perkin-Elmer Spectrum 2000 either in transmission mode or as ATR spectra utilizing a Golden Gate (diamond crystal) accessory from Grasseby Specac. A Leitz Ortholux POL BK II optical polarizing microscope equipped with a Mettler Hot Stage FP 82 central processor was used for studying crystallinity. UV curing was performed on a high power microwave irradiator from Fusion UV Curing Systems, using an electrodeless H-bulb regulated with a P300 power supply. The spectral range used for curing was between 320 and 390 nm. The dose was measured with an Uvicure® Plus device from EIT Inc.

Rheology measurements were carried out on a Rheometrics Dynamic Analyzer RDAII, using parallel plates with a radius of 3.95 mm. Dynamic mechanical properties were analyzed using a Polymer Laboratories dynamic mechanic thermal analyzer (DMTA) in tensile mode.

Synthesis

The synthesis of the semi-crystalline polyester resins is divided into two steps: grafting ε-caprolactone onto the hydroxy-functional hyperbranched polyester and end-capping of the poly(ε–caprolactone)-chains with methacrylate groups, *Figure* 2. *Tables* 1 and 2 present the synthesized polymers and some basic data.

General Procedure for Grafting of Poly(ε-caprolactone) (ε-PCL) Polyesters 1 and 2 Exemplified by the Synthesis of P2G-εPCL(DP=10), 3: 0.96 g (~0.55 mmol hydroxyl groups) of the glassy hydroxyl-functional polyester **1** was ground in a mortar and then added to a two-necked flask equipped with two septa sealed with wires. The polyester was thoroughly dried by at least 10 successive heating (80°C) evacuating cycles whereafter the reaction flask was filled with Ar(g). ε-Caprolactone (10.0 g, 87.6 mmol) and dry toluene (1 ml) were added. The toluene was evaporated under vacuum at 90°C to remove any residual water. After refilling the reaction flask with Ar(g), the temperature was raised to 110°C before a catalytic amount of $Sn(Oct)_2$ was added (one drop). The reaction mixture was stirred for nine hours and eventually became solid. The solid product was dissolved in THF and precipitated into MeOH to give 8.5 g (yield 77 wt%) of a white crystalline powder: ^{1}H-NMR ($CDCl_3$) δ 4.18 (m, -C<u>H</u>$_2$-O-CO-, bis-MPA), 4.04 (m, -C<u>H</u>$_2$-O-CO-, ε-PCL), 3.63 (m, -C<u>H</u>$_2$-OH), 2.29 (m, -C<u>H</u>$_2$-CO-O-, ε-PCL), 1.63 (m, -C<u>H</u>$_2$-CH$_2$-CO-O- or -C<u>H</u>$_2$-CH$_2$-O-CO-), 1.37 (m, -CH$_2$-C<u>H</u>$_2$-CH$_2$-), 1.22 (m, -C<u>H</u>$_3$); ^{13}C-NMR ($CDCl_3$) δ 173.33, 63.94, 62.30, 48.47, 46.40, 33.94, 32.16, 28.17, 25.50, 24.39, 17.60; FTIR (NaCl, cm^{-1}): 3500 (-OH), 1725 (carbonyl).

General Procedure for Methacrylation of the Hydroxy-Functional Polymers 3–6 Exemplified by the Synthesis of P2G–εPCL(DP=10)-MA, 7: 2.5 g of polyester **3**, (~0.13 mmol hydroxyl groups) was dissolved in dichloromethane in a three-necked round-bottomed flask. Triethylamine (0.42 g, 4.2 mmol) and a catalytic amount of 4-dimethylaminopyridine were added to this solution. The flask was equipped with a drying tube and cooled on a water/ice-bath whereafter methacrylic anhydride (0.48 g, 3.1 mmol), diluted with dichloromethane, was added dropwise. The reaction mixture was stirred at room temperature overnight. The reaction mixture was precipitated into MeOH to give 2.4 g (yield 92 wt%) of a white crystalline powder: Mp: 36°C. ^{1}H-NMR ($CDCl_3$) δ 6.07 (s, C=C<u>H</u>$_2$, cis to methyl), 5.53 (s, C=C<u>H</u>$_2$, trans to methyl), 4.18 (m, -C<u>H</u>$_2$-O-CO-, bis-MPA), 4.04 (m, -C<u>H</u>$_2$-O-CO-, ε-PCL), 3.61 (m, -C<u>H</u>$_2$-OH), 2.29 (m, -C<u>H</u>$_2$-CO-O-, ε-PCL), 1.92 (s, -C<u>H</u>$_3$, methacrylate), 1.63 (m, -C<u>H</u>$_2$-CH$_2$-CO-O- or -C<u>H</u>$_2$-CH$_2$-O-CO-), 1.37 (m, -CH$_2$-C<u>H</u>$_2$-CH$_2$-), 1.20 (m, -C<u>H</u>$_3$, bis-MPA); ^{13}C-NMR ($CDCl_3$) δ 173.06, 172.38, 171.69, 166.96, 136.10, 135.35, 125.77, 124.85, 68.48, 63.71, 46.18, 33.73, 27.98, 25.16, 24.21, 17.94; FTIR (NaCl, cm^{-1}): 1725 (carbonyl), 1640 (methacrylate unsaturation).

UV Curing (Crosslinking) of Polyesters 7-10: A mixture of polyester **7**, Irgacure™ 184 (2% w/w) and a small amount of butyl acetate (not more than to dissolve the polyester) was applied with a 700 µm applicator on a glass plate. After evaporating the solvent, the film was melted in the oven at 70°C and then immediately photochemically cured with five subsequent passes under the UV lamp, giving a total dose of 500 mJ cm^{-2}. A part of

Table 2—Synthesized Methacrylated Polyesters 7-10 with Basic Data

Polyester No.	Yield (% w/w)	Degree of Methacrylation[a] (%)
7 P2G–εPCL(DP=10)-MA	92	88
8 P2G–εPCL(DP=30)-MA	96	82
9 P4G–εPCL(DP=10)-MA	97	81
10 P4G–εPCL(DP=30)-MA	96	56

(a) Calculated from ^{1}H-NMR and the calculated DP values

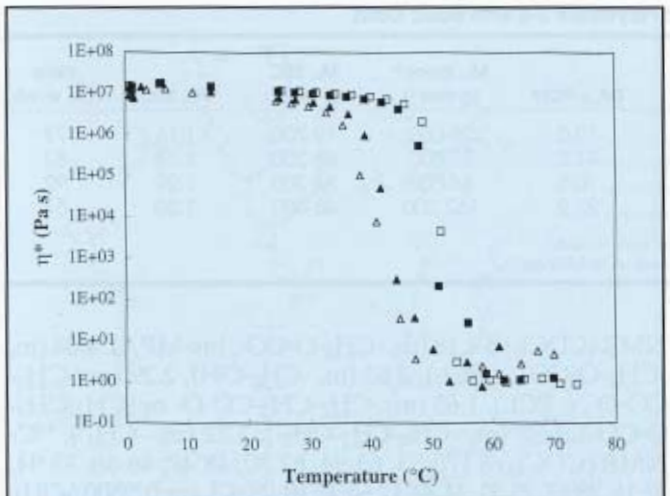

Figure 3—Complex dynamic viscosity (η) as a function of temperature for resins; **7** (Δ), **8** (❑), **9** (▲) and **10** (■), frequency 6.28 rad s^{-1}.*

the film, 1.5*1.5 cm, was covered with a thin glass cover (transparent in the UV range used) giving a section where oxygen inhibition was hindered. Polyesters **7-10** were all cured following the same procedure.

Characterization Techniques

Rheology: The rheological properties of resins **7-10** were determined by measuring the dynamic mechanical shear properties as a function of temperature at 6.28 rad s^{-1}. The samples were melted between the plates at 90°C to obtain a good geometry and then cooled down to 0°C where the temperature scan was started.

Thermal Characterization: The melting/crystallization processes were studied by DSC. DSC scans were performed on polyesters **7-10** both before and after UV curing. The uncured polyesters were studied between 90° and –20°C with a heating/cooling rate of 10°C min^{-1}. All cured polyesters were examined between –70° and 80°C. A heating rate of 10°C min^{-1} was used. The cooling rate was 10 °C min^{-1} from 80° to 0°C and 5°C min^{-1} between 0° and –70°C.

Residual Unsaturation: The residual unsaturation was measured with ATR-FTIR on a diamond crystal. Both uncured and cured resins of polyesters **7-10** were studied. The measurements of the UV-cured films were made by removing the film from the glass plate and measuring both the glass side and the air side of the film. The peak at 1640 cm^{-1}, corresponding to the methacrylate unsaturation, was studied to obtain the amount of residual unsaturation.

Microscopy: The crystallinity of polymers **7-10** was studied both before and after UV curing between 25° and 70°C using crossed polarizers. The UV-cured film was studied on both the glass-covered area and the section exposed to air.

Photo DSC: The curing and melting/crystallization processes were studied by photo-DSC. Polyester **7**, Irgacure 184 (2% w/w) and a small amount of butyl acetate (to dissolve the polyester) were mixed and dried in a vacuum oven to form white crystals. The crystals were studied between –20° and 90°C with a heating/cooling rate of 10°C/min. The curing was performed at 90°C using a total dose of 6 J cm^{-2}. Polyesters **7-10** were all studied following the same procedure.

Dynamic Mechanical Properties: The UV-cured films of resins **7-10** (the air-exposed parts) were removed from the glass plate. The dynamic mechanical properties for 10 × 10 mm of the film samples were examined between –80° and 100°C at 1Hz frequency using auto-strain. The thickness of the films varied between 0.1 and 0.2 mm.

RESULTS AND DISCUSSION

Several aspects have to be considered when designing new solid semi-crystalline resins for thermoset applications. The synthesis must be simple enough and the resin processable with suitable methods producing a stable powder. The crosslinking should be possible to perform with conventional techniques and, finally, the crosslinked film should exhibit the desired properties. Hyperbranched polymers have been shown to exhibit properties that may fulfill some of these demands. Previous work has shown that it is easy to modify the end-groups on hyperbranched polymers to obtain changes of the physical properties.[10-12] Grafting ε-PCL chains to a hyperbranched polyester will result in a semi-crystalline polymer with hydroxyl end-groups. The hydroxyl groups on the polymer can be further modified, e.g., methacrylated, to form a crosslinkable resin.

Synthesis

The hydroxyl-functional aliphatic polyesters used in this study are the only commercially available hyperbranched polymers present today.[13] The polyesters

Table 3—DSC Data for Methacrylated Polyesters 7–10, Before and After Curing

Polyester	ΔH_{curing}[a] (kJ mol^{-1})	ΔH_{melt}[b] Uncured (J g^{-1})	ΔH_{melt}[c] Cured (J g^{-1})	T_m[b] Uncured (°C)	T_g[d] Cured (°C)	T_m[c] Cured (°C)
7 P2G-εPCL(DP=10)-MA	68	40	—	36	–56	—
8 P2G-εPCL(DP=30)-MA	78	67	36	50	–58	33
9 P4G-εPCL(DP=10)-MA	74	44	—	40	–56	—
10 P4G-εPCL(DP=30)-MA	70	64	34	49	–60	36

(a) Photo DSC, curing process, kJ mol methacrylate^{-1}; (b) DSC, 2nd heating, before curing, 10°C min^{-1}; (c) Photo DSC, 2nd heating, after curing, 10°C min^{-1}; (d) DSC, 1st heating, after curing, 10°C min^{-1}.

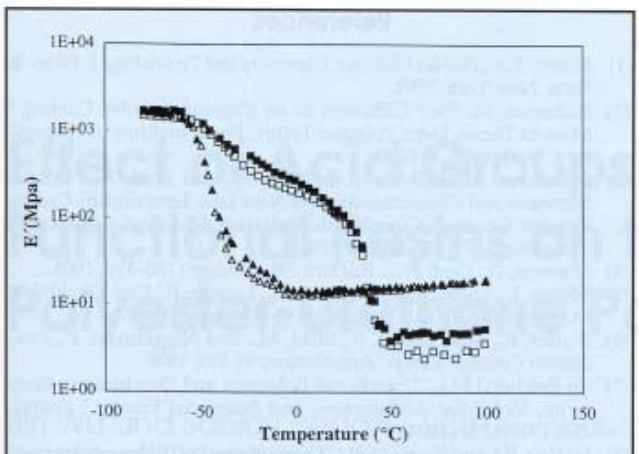

*Figure 4—E´ versus temperature for UV-cured films based on resins **7** (Δ), **8** (❑), **9** (▲) and **10** (■), frequency 6.28 rad s^{-1}.*

are based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA, A_2B-monomer) and ethoxylated pentaerythritol (4-functional core moiety) where the stoichiometric ratio bis-MPA:core determines the molecular weight of the final polymer. The size of the hyperbranched polyester and the length of the PCL-chains are two parameters that can be altered to obtain changes in the properties. Two different sizes of hyperbranched polyesters and two different lengths of the PCL chain ends were chosen for this study giving a total of four different powder coating resins.

Grafting of ε-Caprolactone onto the Hyperbranched Polyesters: ε-Caprolactone was grafted onto the hyperbranched polymers, according to a procedure previously described by Hedrick et al.[12] The polymerization was performed in bulk, and different lengths of the PCL chains were obtained by varying the feed ratio between the polyols and ε-caprolactone. The reaction mixture had to be carefully dried before the initiator was added, since traces of water would initiate homopolymerization of ε-caprolactone.

It has been shown that the ^{13}C-NMR shift of the quaternary carbon in the repeat unit in the polyols is sensitive to the degree of substitution.[13] The quaternary carbon resonates at 50.6 ppm if both hydroxyl groups are left unreacted, at 48.8 ppm if one hydroxyl group remains, and at 46.8 ppm if both hydroxyl groups are reacted. This provides a useful tool to assess the success of the grafting reaction. ^{13}C-NMR spectra of copolymers **3-6** show that the majority of the hydroxyl groups on the hyperbranched polyesters are reacted, although a small fraction of terminal groups remain unreacted.

The ^{1}H NMR spectra of copolymers **3–6** were used to calculate the DP of the PCL grafts as well as the theoretical molecular weight (*Table* 1). The DP was calculated by comparing the integrals of the protons on the methylene adjacent to the hydroxyl end-group relative to the protons on the methylene next to the ester in the repeat unit. The results show that the length of the short chains were close to the length aimed for, while the longer chains differed from the target length. The accuracy of the calculation is reduced at higher DPs, since the peak from the proton close to the hydroxyl groups becomes very small. The interference of the signal from the protons in the hyperbranched core will also affect the calculations, since this signal has shifts similar to the protons on the carbon beside the hydroxyl group. The molecular weights determined by SEC deviate from the values calculated from the NMR data. SEC characterization on highly branched samples is difficult. The separation in the columns is driven by differences in hydrodynamic volume. A linear polymer will have a much larger V_h than the corresponding branched polymer of the same molecular mass. This is in agreement with previous studies[14] which state that SEC underestimates the molecular weight of highly branched polymers when linear polymer standards are used for calibration. Although they are too low, the SEC values will give reasonably accurate information about the polydispersity of the polymers. Polymers **3-6** all have a rather narrow molecular weight distribution, PDI = 1.1 – 1.3.

Methacrylate Functionalization: Attachment of methacrylate moieties to the end groups of polymers **3–6** was readily accomplished by base-catalyzed transesterification using methacrylic anhydride. Air atmosphere and low reaction temperature had to be used in order to prevent premature polymerization, which is always a risk when working with highly functional resins. The degree of functionalization was analyzed by NMR spectroscopy and found to be high (~90%) for all polymers except polymer **6**, which only had about 60% of the end-groups methacrylated (*Table* 2).

Rheological and Physical Properties of Polyesters 7-10 Before Crosslinking: *Figure* 3 shows the complex dynamic viscosity as a function of temperature at 6.28 rad s^{-1} for polymers **7-10**. It is seen that the melting transition, T_m, is lowered for polymers **7** and **9** having short PCL segments. The crystallization of short grafts is more affected by the attachment to the amorphous core compared to the longer grafts. The overall degree of crystallinity is also lower for polymers **7** and **9** since the weight fraction of the amorphous core is larger in the case of short grafts.

Polymers **7-10** are solids up to the melting temperature, T_m, where a rapid drop in viscosity allows film formation without raising the temperature more than 10-20°C above T_m. The viscosity below T_m is high enough to ensure satisfactory storage stability at ambient temperature. Not only the melting point but also the degree of crystallinity is lower for resins **7** and **9** as seen by the DSC measurements presented in *Table* 3. This is expected, since the fraction of PCL-chains by weight is lower for these resins.

Curing Performance of Resins 7-10: Resins **7–10** were photopolymerized in a photo DSC and the results, *Table* 3, show that all resins rapidly cure to high conversions. The enthalpy of polymerization was around 70 kJ mol^{-1} methacrylate in all cases, which is higher than the value found in the literature[15] for polymerization of methyl methacrylate, 57 kJ mol^{-1}. FTIR spectra of films cured under inert atmosphere do not reveal any detectable traces of residual unsaturation. However, a small amount of residual unsaturation, probably due to oxygen

inhibition, was found at the film surface for the samples cured in air. The lack of crosslinking allowed the PCL chains to recrystallize at the surface when lowering the temperature.

Mechanical Properties of UV-Cured Films of Resins 7–10: DMTA studies on the cured films reveal that all samples have a T_g close to –50°C, which is expected for CL-based polymers (*Figure* 4).

The crosslinking reduced the possibility for the PCL chains to crystallize when the films were cooled. Resins **7** and **9**, having short PCL chains, did not crystallize at all in the crosslinked state, while resins **8** and **10**, having longer PCL chains, crystallized to some extent. DSC data in *Table* 3 show that the degree of crystallinity in the crosslinked films of resins **8** and **10** is approximately 50% as compared to before crosslinking. The effect of the crystallization in the network is clearly seen in *Figure* 3, where the films of resins **8** and **10** maintain a higher modulus above T_g as compared to films based on resins **7** and **9**. The modulus dropped above the melting point to a lower level for resins **8** and **10** since these resins have a lower crosslink density. The results show that the structure of the resins has a pronounced effect on the final film properties and that this can be used to tailor a resin for a certain application.

CONCLUSION

It has been demonstrated that semi-crystalline powder coatings based on hyperbranched polyesters can be synthesized. ε-Caprolactone was grafted on hydroxy-functional hyperbranched aliphatic polyesters forming semi-crystalline copolymers. The crystallinity and rheological properties were found to be tailorable by means of the appropriate choice of hyperbranched polyester and the degree of polymerization of the crystalline grafts (ε-PCL). Crosslinkable resins were obtained by methacrylation of the terminal hydroxyl groups. The resins were found to have suitable melt rheology for low temperature powder coatings. All resins were UV cured in the molten state to yield flexible films with low levels of residual unsaturation. The properties of the final crosslinked films were shown to be dependent on the structure of the resins, i.e., long side chains could crystallize in the network producing a semi-crystalline network. Crystallization of short chains was hindered by the crosslinking.

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