

Radiation Curing of Hyperbranched Polyester Resins

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ABSTRACT: A research area that has obtained increasing interest during the last decade concerns improvement of macromolecular properties by changes in the macromolecular architecture. One group of these materials is dendritic polymers, which are highly branched structures exhibiting very different properties compared with linear polymers. One potential application for these polymers is as radiation curable thermoset resins. This article describes a study where the use of an aliphatic hyperbranched polyester as a base for new radiation curable thermoset resins. The hyperbranched polyesters have been characterized with respect to cure rate and final mechanical properties compared with conventional resins. It is shown that hyperbranched polyesters can be used as versatile scaffolds for various radiation curable resin structures. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 612–618, 2000

Key words: radiation curing, thermosets, hyperbranched, acrylate, methacrylate

INTRODUCTION

Radiation curing of thermoset resins is a technique with growing importance for thermoset applications because it offers improvements compared with thermal systems with respect to processing and environmental properties.¹ Radiation curing can be performed with different techniques such as, for example, UV² or high-energy electron beam (EB)³ radiation. UV curing in most cases demands an initiator molecule, which decomposes when it is irradiated with UV light, forming initiating species. The formulation of the resin/initiator mixture must be adjusted to obtain a suitable optical density for the application. Thicker geometries are difficult to cure due to shielding effects unless the initiation system is photobleaching, i.e. the initiator is transformed to species with less absorption in the UV range. EB curing^{4,5} via free radical polymerization differs from UV curing mainly through the initiation process. No initia-

tor is needed in the EB process because the initiating species are formed by cleavage of a bond located on the monomer. This makes the initiation more nonspecific and also leads to a more homogeneous network because the initiation appears evenly throughout the system. The initiating radical is also connected to the binder resin why the efficiency of the crosslinking is slightly enhanced. The main advantage with high-energy electron beams is the possibility to cure thick, up to 2.5 cm, samples. A drawback is higher sensitivity towards oxygen inhibition compared with UV curing.

Another research area that has obtained much attention during the last decade is dendritic polymers, comprising of dendrimers and hyperbranched polymers.^{6–8} Dendritic polymers are a group of polymers made from AB_x-functional monomers giving a backbone structure with numerous branching points. These polymers are also characterized by a large number of end-groups, which greatly affects the properties. Several intriguing properties, such as low solution viscosity and high solubility compared with linear polymers, have been described for these poly-

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mers.^{9,10} Hyperbranched polymers have especially been considered for material consuming applications because they are more easily produced in larger scale compared with dendrimers. Several applications such as rheological additives¹¹ and toughening agents¹² have been suggested for hyperbranched polymers. The use of hyperbranched polymers as thermoset resins^{13–15} have also been described.

This study deals with the use of hyperbranched polyesters as base for new thermoset resins and the applicability of them in radiation curing systems both by themselves and in mixtures with conventional resins.

EXPERIMENTAL

Materials

The hyperbranched polyester, Boltorn, was used as base for the resins and was supplied by Perstorp AB, Sweden. Ebecryl 600 (EB600) was supplied by UCB, Belgium. Irgacure 184 was supplied by Ciba-Geigy. All other reagents were purchased from Aldrich or Lancaster and were used as received.

Equipment

Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FTIR. FT-Raman was recorded on a Perkin-Elmer Spectrum 2000 FT-Raman. Dynamic mechanical properties were measured with a Polymer Laboratories' dynamic mechanical thermal analyzer (DMTA). ¹H-NMR spectra were recorded on a Bruker 250 MHz using CDCl₃ as solvent using the solvent signal as reference.

UV curing was performed either on a Primarc Ltd. MiniCure equipped with two 80-W/cm, medium-pressure Hg-lamps or a Fusion UV Curing System Model F300 equipped with Fusion electrodeless bulbs standard type BF9 (Lamp power 300 W/inch, 1800 Watts total). EB curing was performed with a pulsed sweeping electron beam, which was produced by a microton accelerator with an energy of 6.5 MeV and a current of 80 mA. The dose calibration of the instrument was performed with a Risø calorimeter. The temperature during cure of the thick specimens was measured with a thread thermocouple and recorded by a Combilab equipment from Chipzobit Digitalteknik AB, Sweden.

Table I Data on Polyesters 1–6

Resin No.	M_{theor} (g/mol) (Based Functionality Found by H-NMR)	Methacrylate Functionality (% \pm 5%) (Found by H-NMR)
1	8600	30 \pm 5
2	9300	45 \pm 5
3	9900	60 \pm 5
4	9100	35 \pm 5
5	9100	35 \pm 5
6	9100	40 \pm 5

Synthesis

Synthesis of Methacrylate Functional Hyperbranched Polyesters

Six different hyperbranched polyester resins, 1–6, with different fractions of methacrylate groups as terminal units have been synthesized.

A hydroxyfunctional hyperbranched aliphatic polyester (Boltorn, 4G-OH) based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) as AB₂-monomer and etoxylated (5EO/penta) pentaerytritol (PP50) as core, was used as base for all resins. The polyester had a bis-MPA:PP50 ratio of 60:1 (theoretically 64 OH-groups/molecule) and was used as received. The degree of branching was \approx 0.45 as determined with ¹³C-NMR.¹⁶ More extensive descriptions of the synthesis and characterization of the hyperbranched polyesters are described elsewhere.^{17,18}

Resins 1–6 were all synthesized according to the same general procedure as described for resin 1 below, with the only difference the amount of methacrylic anhydride (Fig. 1). Data on resins 1–6 are listed in Table 1.

Synthesis of Polyester 1. Boltorn, 4G-OH, (30 g, 263.1 mmol-OH), pyridine (12.48 g, 157.9 mmol), and *N,N*-dimethylaminopyridine, DMAP (0.64 g, 5.26 mmol) were dissolved in 100 ml acetone. Methacrylic anhydride (12.17 g, 78.93 mmol) was mixed with 50 ml acetone and slowly added to the reaction vessel. The reaction mixture was left stirring at ambient temperature for 12 h. The completion of the reaction was seen by the disappearance of the anhydride peak (1764 cm⁻¹) in the FTIR spectra of the reaction mixture. The acetone was evaporated and the residue dissolved in 50 ml CH₂Cl₂. The solution was then extracted with 2 \times 20 ml 2M HCl and 2 \times 20 ml 10%

NaHCO₃ solutions. The solution was then dried with anhydrous MgSO₄, filtered, and finally the CH₂Cl₂ was evaporated yielding a clear colorless highly viscous resin.

FTIR (cm⁻¹): 3400 (OH), 1734 (ester carbonyl), 1638 (methacrylate unsaturation). ¹H-NMR* (δ, ppm): 6.1 (–C=CH₂, cis to methyl), 5.6 (–C=CH₂, trans to methyl), 4.2 (–CH₂–O–CO–), 3.7 (–CH₂–OH), 1.9 (–CH₃, methacrylate), 1.2 (–CH₃, bis-MPA). All peaks are broad polymer peaks, hence the inexact shift values. The integrals were used to determine the degree of methacrylation with an accuracy of ±5%.

UV Curing

UV Curing: Comparison Between Different Functionality of the Resin

UV cured films of resins 1–3 were prepared by a general procedure. One gram resin was mixed with 3% (w/w) free-radical photoinitiator (Irgacure 184, 1-benzoylcyclohexanol) and ≈0.5 g acetone. Films of each solution were then drawn on glass plates with a 60 μm applicator and left for 15 min to let the solvent evaporate. The films were then cured by 10 successive passes through the MiniCure with a band speed of 12.4 m min⁻¹.

UV Curing: Effect of Dose and a Comparison Between Resin 4, EB600, and Mixtures Thereof

UV-cured films of resin 4, EB600, and a 50/50 (w/w) mixture of resin 4 and EB600 were prepared by a general procedure.

The resins were mixed with 4% (w/w) Irgacure 184 as initiator and 20% (w/w) solvent (acetone or butyl acetate). Films were then drawn on a glass plate using a 60-μm applicator and left for 15 min to allow the solvent to evaporate. The UV curing of samples were then performed with the Fusion lamp at a band speed of 25.2 m min⁻¹ corresponding to a dose of 100 mJ cm⁻² per pass. Films cured with 100, 200, 300, 400, or 500 mJ cm⁻² respectively were prepared of each mixture. The final film thickness was 30 ± 5 μm.

EB Curing

Thin Films

EB-cured films of resin 5, EB600, and a 50/50 (w/w) mixture of resin 5 and EB600 were prepared by a general procedure.

The samples were mixed with 50% (w/w) of butyl acetate and films drawn on glass plates

with a 60-μm applicator and left for 15 min to allow the solvent to evaporate. The films were then EB-cured by four successive sweeps of 25 kGy each, giving a total dose of 100 kGy. Samples of all cured films were removed with a scalpel in order to measure the different film properties.

Thick Samples

Three different mixtures containing EB600 and 0, 10, or 20% (w/w) of resin 6 were prepared and cured as thick samples. The mixtures were placed in 14-ml glass vials (φ 2 cm) and cured from the side by four successive sweeps of 25 kGy each, giving a total dose of 100 kGy. The temperature during cure was monitored with a thread thermocouple placed in the center of the sample. Test specimens for mechanical testing (2 × 2 × 40 mm) were cut from the center of the cylinder.

Characterization of Cured Samples

Residual unsaturation was determined with FT-Raman spectroscopy monitoring the unsaturation peak at 1635 cm⁻¹. The mechanical properties of the films were measured in tensile mode with a DMTA at a frequency of 1 Hz and a heating rate of 2°C min⁻¹. The test specimens from the thick samples were studied with a double cantilever geometry.

RESULTS AND DISCUSSION

Synthesis

The results show that it is relatively easy to make resins with different functionality based on the same base polyester. The methacrylation of the hyperbranched polyester worked well when low fractions of methacrylation were aimed for, i.e. 30%. The conversion was reduced when aiming for larger fractions of end-groups modified to methacrylates, probably due to steric hindrance. The main problem arose in the purification step where the two phases were difficult to separate in the extraction step, resulting in poor yields. The reproducibility of the synthesis is limited to ±5% as seen when comparing two identical batches. This also resulted in subsequent differences in mechanical properties of the cured films. Premature gelation is also a risk when increasing the functionality.

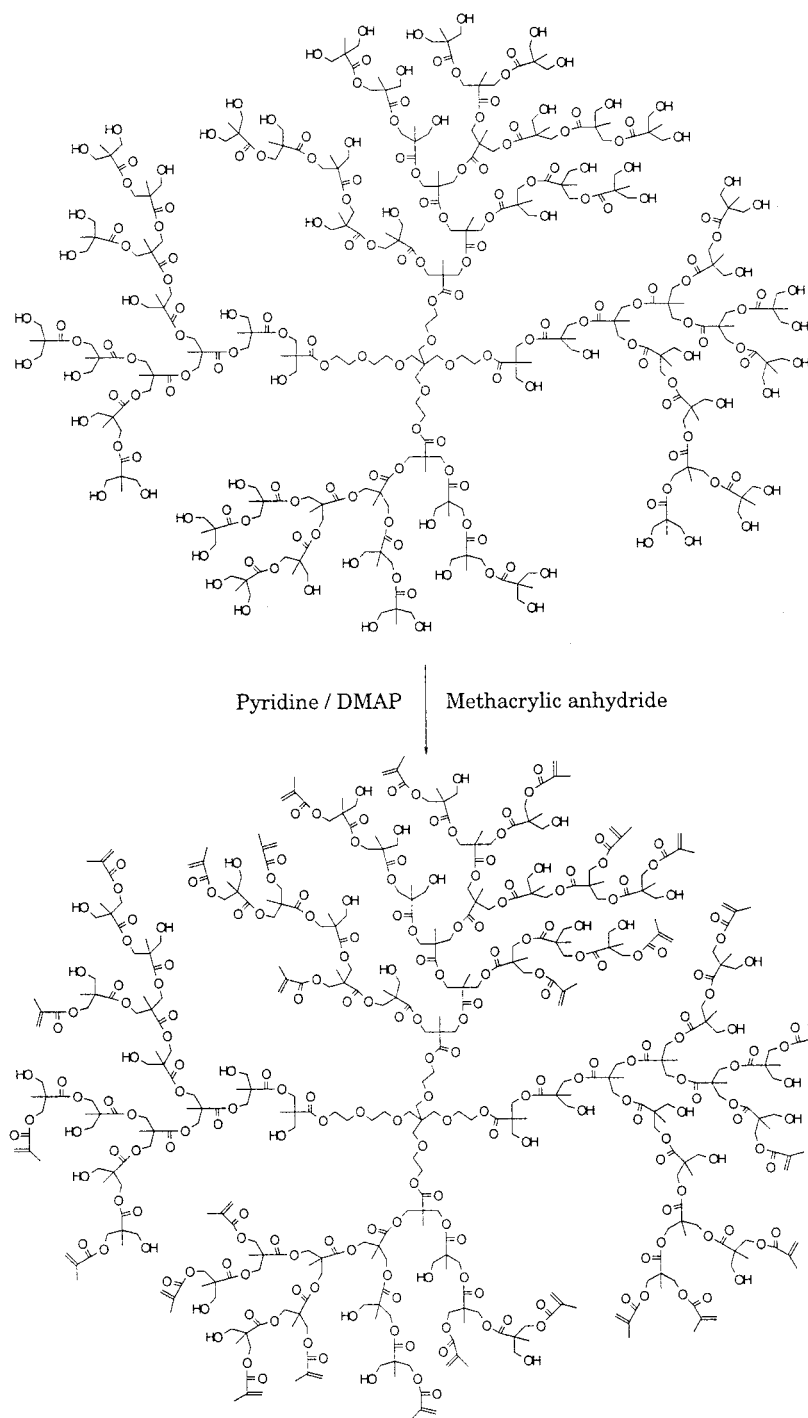


Figure 1 Schematic description of the resin synthesis.

UV Curing: Comparison Between Different Functionality

Very different network properties can be obtained for resins based on the same hyperbranched polyester as backbone of the resin as seen by a comparison of cured resins **1**, **2**, and **3** in Figure 2.

The T_g , measured as the $\tan(\delta)$ -peak value, increases from 110°C for resin **1** to 160°C for resin **3** at the same time as the transition becomes wider. This indicates that a higher crosslink density is obtained when increasing the functionality, but also indicates that the network becomes more

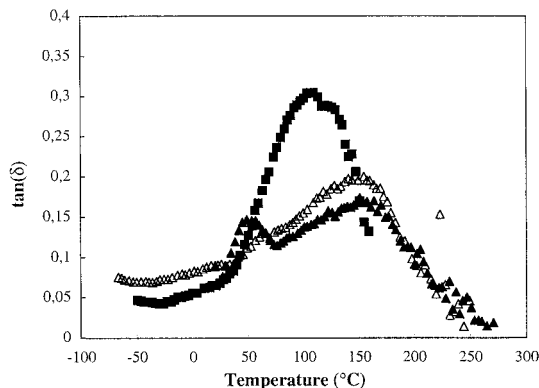


Figure 2 E' versus temperature for UV-cured films of resins **1** (■), **2** (△), and **3** (▲).

inhomogeneous. The amount of residual unsaturation also increases from 5% for resin **1** to 20% for resin **2** and 30% for resin **3**. This can be attributed to reduced mobility of the methacrylate groups with increasing T_g , i.e. with increased functionality. A small amount of postcuring during the DMTA-scan can be seen for resin **3** as a peak in the curve above ambient temperature.

UV Curing: Effect of Dose

A more extensive study on UV curing of resin **4** was performed to see how this kind of resin behaved with respect to property evolution as a function of dose and in homogeneous mixtures with conventional resins. Resin **4** was cured pure and in mixtures with a conventional acrylate resin, EB600, which is an acrylated glycidyl ether of bis-phenol-A.

Figure 3 presents the amount of residual un-

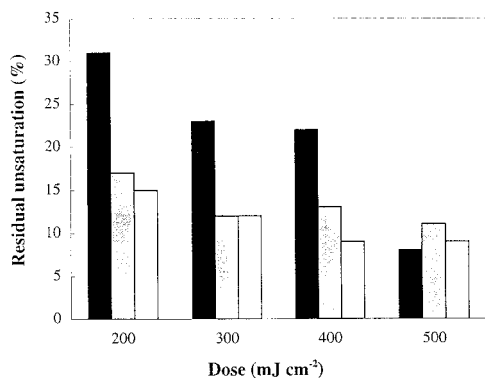


Figure 3 Residual unsaturation versus dose for mixtures different pure resin **4** (white), a mixture of resin **4** and EB600 (50/50, w/w) (gray), and pure EB600 (black).

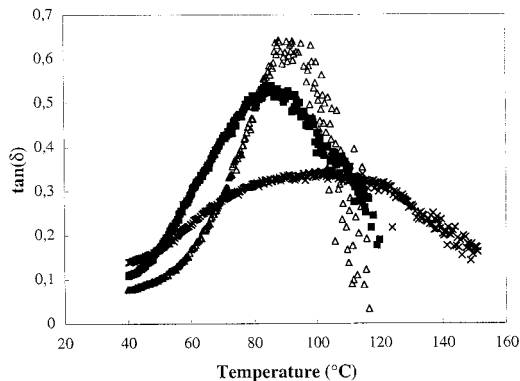


Figure 4 $\text{Tan}\delta$ versus temperature for UV-cured films based on different resins; pure resin **4** (×), a mixture of resin **4** and EB600 (50/50, w/w) (■), and pure EB600 (△).

saturation as a function of dose for either pure resin **4**, a mixture of 50% resin **4** and 50% EB600, or pure EB600. It is shown that the rate of polymerization is as fast as, or even faster for samples containing resin **4** compared with pure EB600. All samples have however a similar final amount of residual unsaturation. The results show that although resin **4** is a methacrylate, it cures at a comparable rate to an acrylate. The fast crosslinking of the hyperbranched polymer indicate that the end-groups are highly accessible for polymerization and not trapped in the network.

Cured films of EB600 present a narrow T_g -transition above ambient temperature as seen in Figure 4. The polymerization is limited by vitrification effects, i.e. the mobility of the nonreacted acrylate groups is reduced at a certain point of crosslinking. The mixtures containing resin **4** exhibit a much wider transition, i.e. a much more polydisperse network. It can be speculated that the methacrylate end-groups in this network structure can react easier with other groups either intra- or intermolecularly.

EB Curing

EB-cured films of resin **5**, EB600, and a 50/50 (w/w) mixture of resin **5** and EB600 exhibit a similar behavior to the UV-cured samples with the difference that the transitions are shifted slightly upwards in temperature (Figure 5). The nature of EB-curing allows for a small additional amount of crosslinking because the initiating radical is formed from the resin itself rather than from an added initiator.

EB-curing can, however, easily be performed on much thicker samples to obtain a different

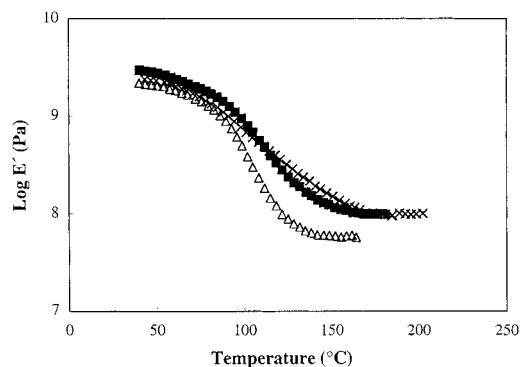


Figure 5 E' versus temperature for EB-cured films based on different resins; pure resin **5** (\times), a mixture of resin **5** and EB600 (50/50, w/w) (\blacksquare), and pure EB600 (\triangle).

thermal history. It has been shown previously that the sample geometry has a large effect of the final properties of the crosslinked polymer.¹⁹ The sample geometry will have an effect on the heat dissipation rate from the sample, i.e. the reaction heat will induce a temperature rise which in the case of a thick specimen will be higher than in the case of a thin sample.

Samples of pure EB600, a 90/10, and an 80/20 (w/w) mixture of EB600 and resin **6** were EB-cured as thick specimens while monitoring the temperature to see the effect of temperature on the final properties. Figure 6 shows the temperature during cure in the thick specimens. The results show that the temperature rises steeply after the first sweep and reaches a level of 160°C for pure EB600 and lower with increasing amount of resin **6**. The reduction in maximum temperature (T_{\max}) with increasing amount of resin **6** can be

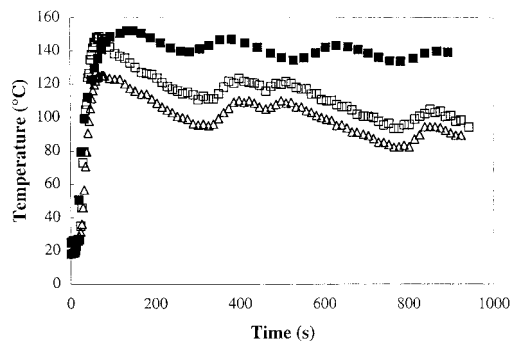


Figure 6 Temperature during cure of thick specimens of different resins; pure EB600 (\blacksquare), a mixture of resin **6** and EB600 (10/90, w/w) (\square), and a mixture of resin **6** and EB600 (20/80, w/w) (\triangle).

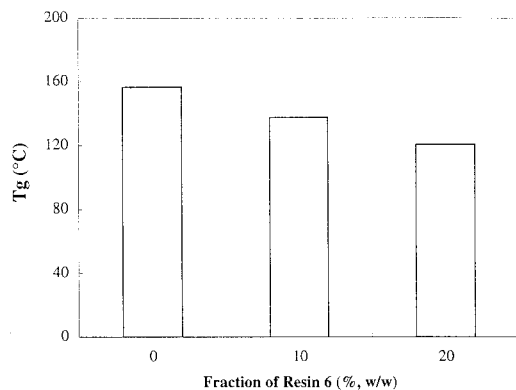


Figure 7 T_g versus fraction of resin **6** in mixtures with EB600.

explained by the lower reaction enthalpy for methacrylates compared to acrylates.²⁰ The maximum temperature in all cases exceeds the T_g of the formed polymer why vitrification effects can be assumed to have less importance for thick specimens.

Figure 7 shows the T_g for the different bulk samples as determined by the $\tan\delta$ peak value. The T_g for pure EB600 has increased significantly, from 110 to 155°C, when compared with the film geometry. When blended with hyperbranched resins, the T_g of the cured sample decreased, which is the opposite of the behavior noticed for blends cured as films. The hyperbranched resins reached a high conversion in all geometries, whereas EB600 had to be cured as a thick specimen to obtain full cure. Therefore, the softening effect was not seen in the case of thin film geometries because EB600 had not reached full cure. The amount of residual unsaturation was around 6% in all thick samples, i.e. close to the detection limit, which also confirms the high degree of cure. The aliphatic backbone of the hyperbranched resin induces a softening of the system, which is seen when comparing systems with the same amount of cure.

CONCLUSIONS

It has been shown that hyperbranched polyesters are versatile scaffolds for the synthesis of hyperbranched methacrylate functional polyester resins for radiation curing (UV or EB). Very different properties can be obtained by varying the functionality of the hyperbranched resins. The hyperbranched resins polymerize readily with small

amounts of residual unsaturation after curing. The methacrylate end-groups are accessible for polymerization, i.e. they have enough mobility to react to a high conversion. The networks based on hyperbranched resins are inhomogeneous compared with networks formed on a conventional difunctional monomer (EB600).

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