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Hyperbranched aromatic epoxies in the design of adhesive materials

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Summary

The use of hyperbranched aromatic epoxy polymer **2** (HARE) as a component in various adhesion experiments has been demonstrated. Two different modes of curing were tested, including a photoinitiated cationic curing process and a polyfunctional amine curing process. These processes gave flexible films that showed good adhesion to nylon, steel, and glass. Furthermore, blends of HARE and the commercial epoxy resin bisphenol F diglycidyl ether (BPFG) were cured with 2-ethyl-4-methylimidazole (EMI) at 150 °C on lap-shear assemblies. These cured assemblies displayed adhesive strengths in the range of 15 MPa over a broad range of HARE/BPFG weight ratios.

Introduction

The demand for polymeric materials with novel or improved properties relative to existing materials requires the synthesis and properties evaluation of polymers that possess unique structural features. Dendritic polymers (1) clearly fall into such a category. The unusual properties of dendrimers, relative to linear polymers, result from their highly branched structure, globular shape, and multiplicity of chain-ends. However, the preparation of dendrimers is highly demanding in terms of synthetic effort, purification, and ultimately expense. Thus, dendrimers are best suited for high value added or extremely high performance applications such as targeted drug delivery (2) or nanoscale electronics (3).

Hyperbranched polymers (HBP's) share some of the structural and physical properties of dendrimers, but HBP's are much more readily accessible synthetically (4). Hyperbranched polymers are generally prepared from AB_n-type monomers (n usually ≥ 2) in a one-step polymerization. While the degree of branching and structural precision of hyperbranched polymers are considerably lower than those of dendrimers, HBP's possess a practical competitive advantage for potential commercialization, due to the lower cost that is derived from simpler preparations. Some applications of HBP's reported already include the use of hyperbranched polyphenylenes as rheology modifiers for polystyrene (4b), and hyperbranched polyesters as toughening components in epoxy resins (5) and as processing additives in polyethylene extrusion (6). Herein we report our initial efforts to apply hyperbranched polymers, specifically hyperbranched aromatic epoxies, to adhesion (7), an area with numerous bulk and specialty applications. We rationalized that a hyperbranched polymer containing multiple chain-end epoxide substituents might hold promise as a functional material in epoxy formulation and curing, perhaps including the adhesion requirements involved in microelectronics packaging.

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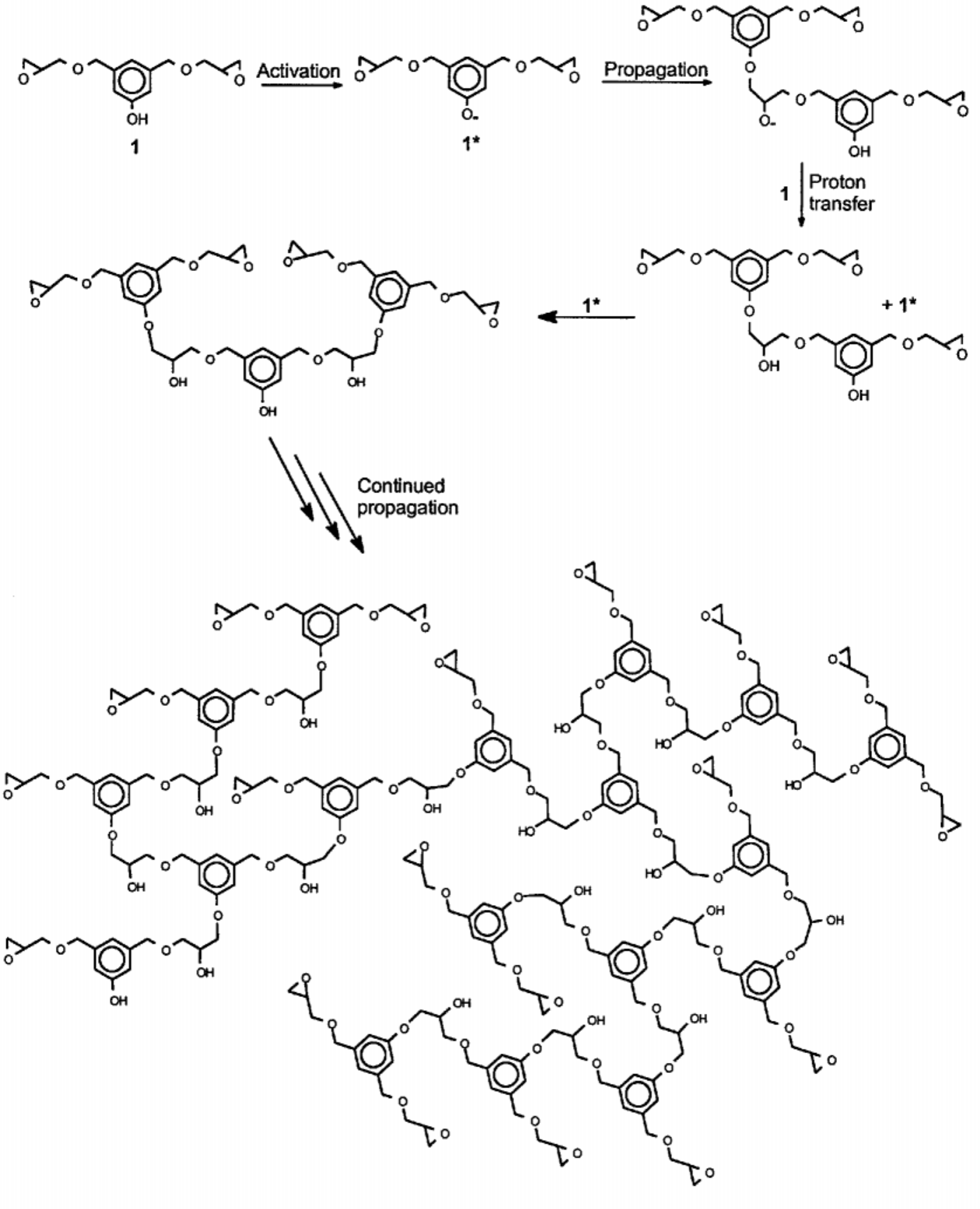
Synthesis of hyperbranched aromatic epoxy 2 (HARE)

The original synthesis of hyperbranched aromatic epoxies has already been reported by Chang and Fréchet (8), who used a base catalyzed proton transfer polymerization to generate the desired hyperbranched aromatic epoxy from AB_2 monomer **1**, a diepoxy phenol. The polymerization mechanism is depicted in **Scheme 1**.

Scheme 1



Hyperbranched aromatic epoxy (HARE) **2**

The key features of the polymerization process include 1) propagation by addition of nucleophilic phenoxide ion of one monomer to an epoxide substituent of another, and 2) rapid proton transfer to convert the secondary alkoxide generated in the nucleophilic addition step to the secondary alcohol, with concomitant formation of another nucleophilic phenoxide. Continued propagation in this manner gives the desired hyperbranched aromatic epoxy polymer (HARE) **2**. The hyperbranched aromatic epoxy used in the adhesion studies had a molecular weight (M_w) of 7,600 (DP = 28) and epoxy equivalent weight (EEW) of 269 (9).

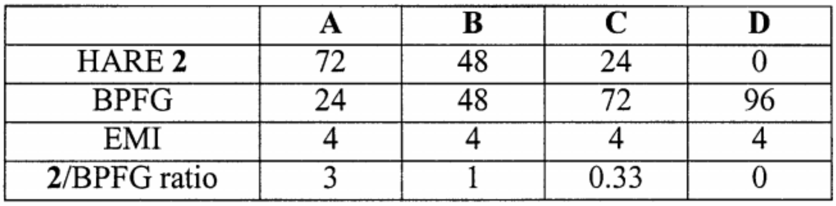
Adhesion studies

Qualitative studies intended to test the suitability of these hyperbranched aromatic epoxies as materials for adhesion applications proved promising. The curing compositions chosen for the initial experiments included the use of a commercial sulfonium salt latent acid photocationic catalyst, Cyracure UVI-6974 (10), as well as various amine/epoxy formulations to be described. The sulfonium catalyst showed good solubility in the hyperbranched polymer at 1.4 weight percent, and exposure of this formulation to UV light (365 nm, 30 mw/cm^2) for 180 seconds gave a dry, elastomeric film. Faster cure-speed was observed when a bis-cycloaliphatic monomer, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ECEC) and a higher level of sulfonium salt catalyst were used in the formulation. Thus, a composition consisting of equal weights hyperbranched polymer and ECEC, and containing 4.8 weight percent sulfonium salt gave a dry flexible film after 60 seconds UV irradiation. This curing process gave films that displayed good adhesion to glass, as well as good flexibility. The later point is especially noteworthy, as most conventional photocured epoxy materials are brittle in nature.

Further adhesion studies involved the investigation of polyoxypropylene diamine (Jeffamine 230) for its potential as an amine curing resin in formulations with hyperbranched aromatic epoxy **2**. Unfortunately, the Jeffamine-based composition cured very slowly, thus a full adhesive assessment was not performed. However, an alternative amine based formulation consisting of 3:2 parts by weight of **2** and a low molecular weight polyethyleneimine gave much better results. The combination of this branched amine with hyperbranched epoxy **2** resulted in rapid curing (ca. 20 minutes) at room temperature. This gave a rubbery material that showed good adhesion to nylon, steel, and glass in qualitative lap-shear assessments.

The initial results described above led us to perform a quantitative adhesive strength evaluation of compositions containing hyperbranched aromatic epoxy (HARE) **2**. This was done by testing formulations consisting of **2** blended with various amounts of bisphenol F diglycidylether (BPFG), a low viscosity epoxy resin (11). 2-Ethyl-4-methylimidazole (EMI, 4 wt. %) was employed as the reactive catalyst to promote curing. The four compositions (**A-D**) of HARE/BPFG weight ratios studied are shown in **Table 1**. Composition **D**, containing no hyperbranched polymer, was included in the study for comparative purposes. While blends of HARE and BPFG showed signs of phase separation at room temperature, they were completely compatible at elevated temperatures. Composition **A**, containing the highest percentage of hyperbranched polymer, had a pasty appearance, while mixtures **B-D** were viscous liquids. This reflects the lower viscosity of BPFG relative to HARE (essentially a solid under ambient conditions).

Table 1. Composition of adhesive formulations A-D consisting of hyperbranched aromatic epoxy (HARE) **2** and BPFG.

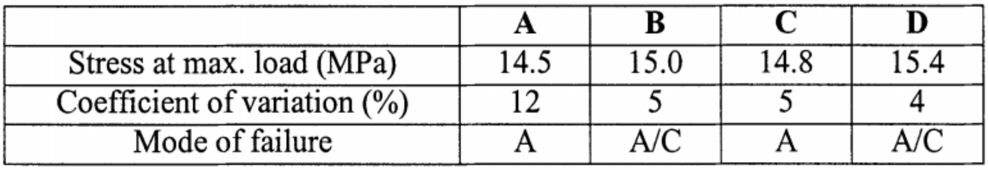


	A	B	C	D
HARE **2**	72	48	24	0
BPFG	24	48	72	96
EMI	4	4	4	4
2/BPFG ratio	3	1	0.33	0

The experimental design for these quantitative adhesion studies employed rectangular mild-steel lap-shear substrates (101.6 x 25.4 x 1.6 mm^3) that were degreased and grit-blasted prior to performing the adhesion experiments. To assemble the lap-shear adhesive joints, the end of one side of a substrate was coated over its entire area with a thin film of blended adhesive. This coated substrate was then degassed (3 minutes at 20 Torr) at ambient temperature to remove air bubbles. The second substrate, which was not coated, was then pressed into the coated substrate to create an overlapping joint, with an area of 25.4 x 12.7 mm^2. This overlap assembly was secured with spring clamps, then heated at 150 °C for 1 hr to promote curing. The assembly was then allowed to stand at room temperature for 24 hrs, followed by an adhesive strength evaluation using a tension tester (ASTM D1002). The results of these tension measurements are shown in **Table 2** (12).

The adhesive strength values observed for HARE-containing compositions **A-C** were comparable to those obtained with the conventional epoxide monomer used in composition **D**. Lap-shear strength values for conventional amine cured epoxies are typically in the range of 18-24 MPa (11). The slightly higher statistical variation observed for composition **A** may be due to incomplete evacuation of air bubbles from the composition, which were incorporated during the blending operation. Visual examination of the debonded specimens showed failure predominately at the adhesive interface, although a few substrates from compositions **B** and **D** showed signs of both adhesive and cohesive failures. This suggests that use of specific adhesion promoters and/or surface treatments should enhance the strength of the hyperbranched polymer containing adhesive materials.

Table 2. Lap-shear adhesive strength measurements of HARE-BPFG blends, reported as an average of five measurements. Strain rate = 1.27 mm/min; A = adhesive failure; A/C = adhesive and cohesive failure.



	A	B	C	D
Stress at max. load (MPa)	14.5	15.0	14.8	15.4
Coefficient of variation (%)	12	5	5	4
Mode of failure	A	A/C	A	A/C

The data in **Table 2** indicates that increasing the concentration of HARE in the epoxy formulation does not correspond to a loss of adhesive strength in the cured material. This is significant as it suggests that functional hyperbranched polymers may be used as reactive additives in epoxy formulations without the risk of reduced adhesive properties that could result from the formation of localized microgels (13). Such inhomogeneities are known to occur by intramolecular addition reactions that occur during the polymerization of multi-functional epoxides and acrylates in highly crosslinked systems, and are believed to have an important influence on the thermal and mechanical properties of crosslinked polymers (13,14)

In summary, the ability of a hyperbranched aromatic epoxy polymer to function as an effective component in adhesive formulations has been established. As a result of this study, one can speculate that future investigations of this type might better employ lower viscosity hyperbranched epoxies. This may require the preparation and properties evaluation of hyperbranched aromatic epoxies of lower molecular weight, or perhaps the use of hyperbranched epoxy resins containing non-aromatic material in the polymer backbone.

Acknowledgements

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Experimental

Preparation of hyperbranched aromatic epoxy 2. A solution of **1** (27.07 g, 101.8 mmol) and Bu_4NCl hydrate catalyst (1.41 g, 5.09 mmol) in dry THF (86 mL) was stirred at 60 °C for 80 hrs under nitrogen. Polymer growth was monitored by GPC analysis (against polystyrene standards) on THF solutions of samples withdrawn from the reaction mixture. The mixture was then removed from the heating bath, diluted with THF (50 mL), and precipitated into MeOH (2 L). The methanol was decanted, and the polymer product dried *in vacuo* to give a colorless, sticky material (20.5 g, 76%): GPC: M_w 7,600, M_n 3,600; ^1H NMR (500 MHz, $CDCl_3$) δ 6.83 (br, CH, aromatic), 4.92 (br, $ArCH_2O$, polymer backbone), 4.15-3.35 (br, CH and CH_2, polymer backbone), 3.16 (CH, epoxy), 2.77 (C*H*H, epoxy), and 2.57 (CH*H*, epoxy) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 139.7, 119.4, 113.0, 73.1, 72.9, 71.2, 70.9, 69.0, 50.8, and 44.2 ppm; Anal. Calcd. for polymer prepared from $C_{14}H_{18}O_5$ monomer: C, 63.15; H, 6.81; Found: C, 63.04; H, 7.00.

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9. Calculation of epoxy equivalent weight: 43/0.16 = 268.75. 43 = weight of epoxy group; 0.16 = weight percent of epoxy in polymer (taken as ½ of the weight percent of epoxy in the monomer).

10. Cyracure UVI-6974 is a solution of triarylsulfonium hexafluoroantimonate salts in propylene carbonate supplied by Union Carbide.

11. BPFG is a relatively low viscosity epoxide functionalized phenol formaldehyde resin containing the monomer BPFG as the main component. For a reference to this material see, Adams L, Gannon J. (1986) Encycl. Polym. Sci. Eng. 2nd ed., Klingsberg A, Muldoon J. Eds.: Wiley & Sons, N. Y., Vol 6.

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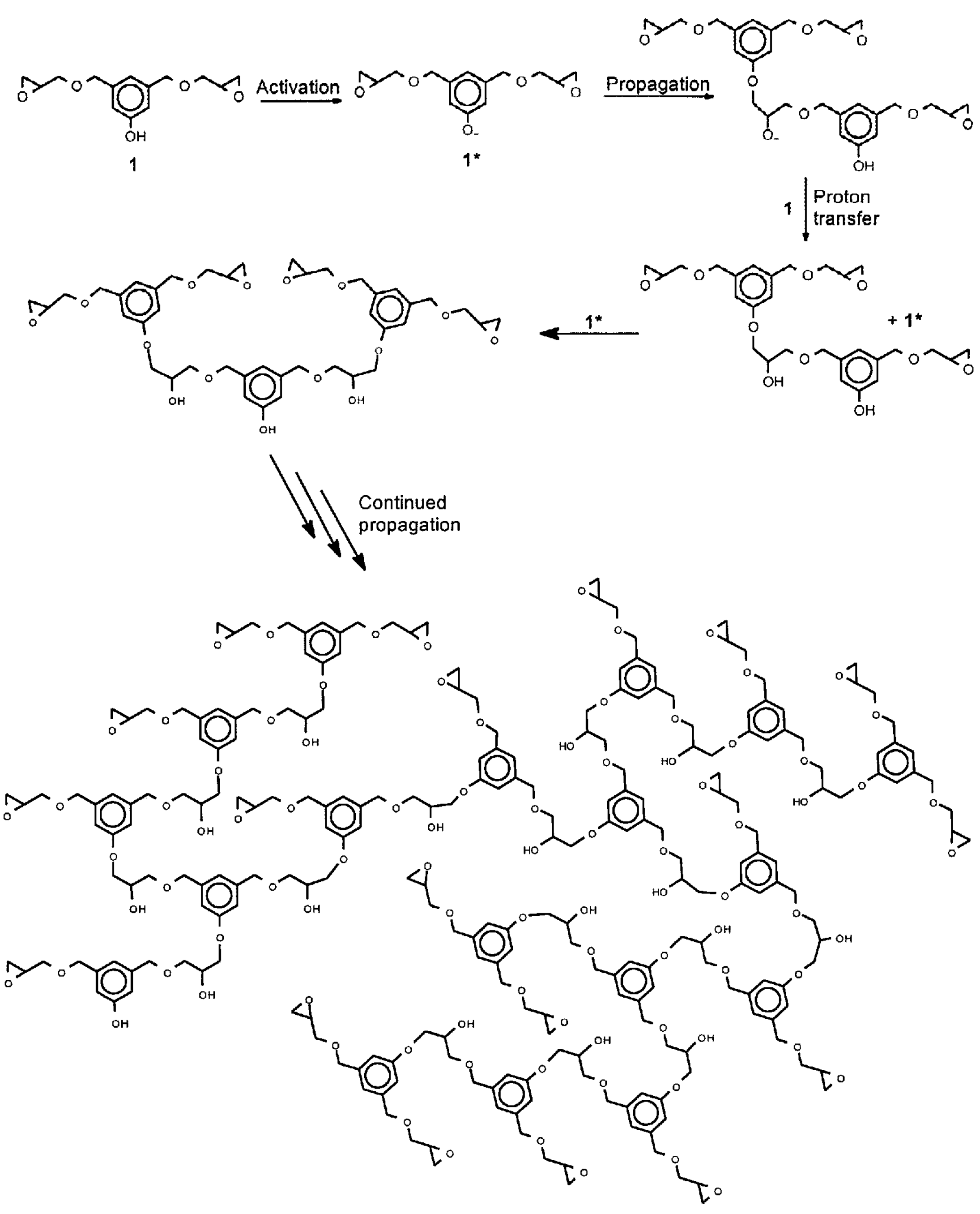

Hyperbranched aromatic epoxy (HARE) **2**