

HYPERBRANCHED EPOXY RESINS PREPARED BY PROTON TRANSFER POLYMERIZATION FROM AN $A_2 + B_3$ SYSTEM*

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Abstract Epoxy-terminated hyperbranched polymers (EHBPs) were prepared by proton transfer polymerization and characterized by FT-IR, ^1H -NMR and GPC. The solution and thermal properties of the uncured samples and mechanical properties of cured samples were examined. The thermo-stable products had good solubility in polar solvents, low solution viscosity and T_g s ranging from 15°C to 33°C depending on their molecular weights. The mechanical properties of cured films were studied and compared with those of a bisphenol-A type epoxy resin. The films of EHBPs had good impact resistance and high gloss values without sacrificing hardness and adhesion.

Keywords: Hyperbranched; Epoxy; Proton transfer polymerization.

INTRODUCTION

The synthesis of tailored dendrimers and hyperbranched polymers (HBPs) has attracted considerable attention in recent years^[1–5]. Compared with dendrimers, HBPs have lower branching efficiency. However, both of them still show many interesting similarities in structure and properties such as good solubility, low melt and solution viscosity, high density of peripheral functionalities and absence of entanglement. In addition, HBPs can often be synthesized by simple one-step polymerization, making their use in engineering applications more economically viable^[6].

Fréchet *et al.*^[7–11] reported the preparation of hyperbranched polyethers and polyesters with epoxide ends and internal hydroxyl functionalities from AB_n and $A_2 + B_3$ monomers *via* proton transfer polymerization. Compared with the conventional way of preparing epoxide hyperbranched polymers^[12–16], in which the hyperbranched cores were synthesized and purified first and then the epoxy terminals were introduced, proton transfer polymerization provides a facile way to obtain hyperbranched epoxy resins. Hyperbranched structure and epoxide terminals can be obtained in a one-pot procedure by the method of proton transfer polymerization. Access to AB_n monomers involves synthetic effort, which is potentially problematic, especially on a large scale. Epoxide hyperbranched polymers from $A_2 + B_3$ monomers reported by Fréchet *et al.*^[7, 8] may have limited uses in engineering application because of their aliphatic backbone, especially as bulk resins. So, epoxide aromatic hyperbranched polymers from the wider commercial available bi- and trifunctional monomers possess a practical competitive advantage for potential commercialization due to their improved properties and lower cost derived from simpler preparation. More interestingly, it was found that proton transfer polymerization could be

* This work was financially supported by the Natural Science Foundation of Beijing (No. 2092023) and the Program of Introducing Talents Discipline to Universities (No. B08003).

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Received March 10, 2010; Revised April 20, 2010; Accepted April 22, 2010

doi: 10.1007/s10118-011-1034-x

used to prepare hyperbranched epoxy resin with structure most close to the conventional bisphenol-A type epoxy resin (BAER) through appropriate choice of starting monomers.

BAER is the most widely used epoxy resin and one of the most important industrial materials because of its excellent adhesion, good thermal and mechanical properties^[17, 18]. Preparation of its corresponding hyperbranched variance would allow material evaluation of an unconventional type of epoxy polymers. It is expected that the new kind of polymer can not only retain the properties of its linear one but improve other properties due to its hyperbranched architecture. To our knowledge, there are no reports on hyperbranched epoxy resins structurally similar to BAER.

In this work, novel epoxy-terminated hyperbranched polymers (EHBPs), analogue to BAER, were synthesized. Bisphenol-A (BPA) and trimethylolpropane triglycidyl ether (TMPTG), both commercially available, were used as A_2 monomer and B_3 monomer, respectively. Thermal behaviors of the resultant hyperbranched polymers were studied. Solution behavior and film properties were also investigated and compared with those of BAER.

EXPERIMENTAL

Materials

BPA and tetrabutylammonium bromide (TBAB) were purchased from FuChen Chemical Factory, Tianjin, China. TMPTG was supplied by XinYuan Chemicals Co., Ltd., Anhui, China. Phenol diamine modified with cashew nutshell oil (NX-2041 from Cardolite, America) with an amine weight equivalence of 82 g/mol was used as the curing agent. E20, BAER of epoxide value 1.9–2.1 mmol g⁻¹, was purchased from ChenGuang Chemical Institute, Sichuan, China. Other materials were purchased from Beijing Chemical Factory, China. All chemicals were used as received.

Synthesis of EHBP

A typical polymerization procedure goes as follows (sample 1 in Table 1): BPA (4.56 g, 20 mmol), TMPTG (6.30 g, 20 mmol), TBAB (0.31 g, 1 mmol) and 40 mL THF were mixed in a sealed flask and stirred at 68°C for 22.5 h under nitrogen. The reaction vessel was then removed from the heating bath and cooled to room temperature. The mixture was diluted with THF (20 mL) and precipitated into methanol (500 mL). This process was repeated again. The solvent was decanted, and the polymer product was subsequently dried under vacuum to give a colorless solid material (7.6 g, 70%). ¹H-NMR (DMSO): δ = 0.765 (broad, CH₃), 1.28 (broad, CH₂), 1.541 (s, Ph—C(CH₃)₂—Ph), 2.512 (broad, CH₂, epoxy ring), 2.625 (broad, OCH₂, glycidyl), 3.000 (broad, OCH, epoxy), 3.262–3.899 (m, OCH₂, CH(OH)), 4.960, 5.029 (d, OH), 6.631–7.068 (d, CH, phenyl). IR (KBr): 3500 cm⁻¹ (s, OH), 2945–2870 cm⁻¹ (s, CH), 1633–1515 cm⁻¹ (s, aromatic ring), 1248–1184 cm⁻¹ and 1075–1010 cm⁻¹ (s, COC), 908 cm⁻¹ (w, epoxy ring).

Preparation of EHBP Films

5 g EHBP (sample 2 in Table 1), 0.82 g NX-2041 and 10 g xylene/*n*-butanol mixture ($V/V = 7/3$) were mixed and stirred to form a homogeneous low viscosity solution, then brushed the mixture onto the polished mild steel strips with a size of 70 mm × 30 mm × 0.3 mm. The coated strips were dried in the air for 10 h and in a 60°C vacuum oven for 7 h. Physical-mechanical tests were carried out after conditioning the coated strips at room temperature for 24 h. For comparative studies, a control experiment was carried out with E20 and a stoichiometric amount of NX-2041.

Characterization Methods

The ¹H-NMR spectra were recorded on an AVANCE 600 spectrometer (Bruker, Germany) using deuterated dimethyl sulfoxide (DMSO-d₆) as a solvent. The FT-IR spectra were obtained with a Thermo Nicolet Impact 210 FT-IR spectrophotometer using KBr pellet. Gel permeation chromatography (GPC) was performed on a Waters GPC 515-2410 system equipped with a RI detector and packing column (Waters Styragel HT3-5-6E). Tetrahydrofuran (THF) was used as the mobile phase. The apparatus was calibrated with linear polystyrene

standards. DSC was carried out on a Pyris 1 DSC instrument under nitrogen at a heating rate of 20 K/min with a gas flow of 20 mL/min. TGA was measured using a Perkin-Elmer TGS-2 thermogravimetric analyzer at a heating rate of 10 K/min under nitrogen.

The viscosities were measured using a DV-1 spinning viscometer (Shanghai Instrument Co., Shanghai, China) at 30°C. The hardnesses of films were measured on a QHQ pencil tester (Tianjin Instrument factory, Tianjin, China). The impact tests were carried out on a QJL impact tester (Tianjin Instrument factory, Tianjin, China), and the height of the free fall (weights 1000 g) at which the paint film still remained undamaged was recorded. Adhesion was measured using a QFD adhesion tester (Tianjin Instrument factory, Tianjin, China). The degree of gloss was measured by a BYK Gardner (micro-TRI-gloss) at 60°. Coatings thickness was obtained from a coating thickness gauge BYK-test 7500 (Germany).

RESULTS AND DISCUSSION

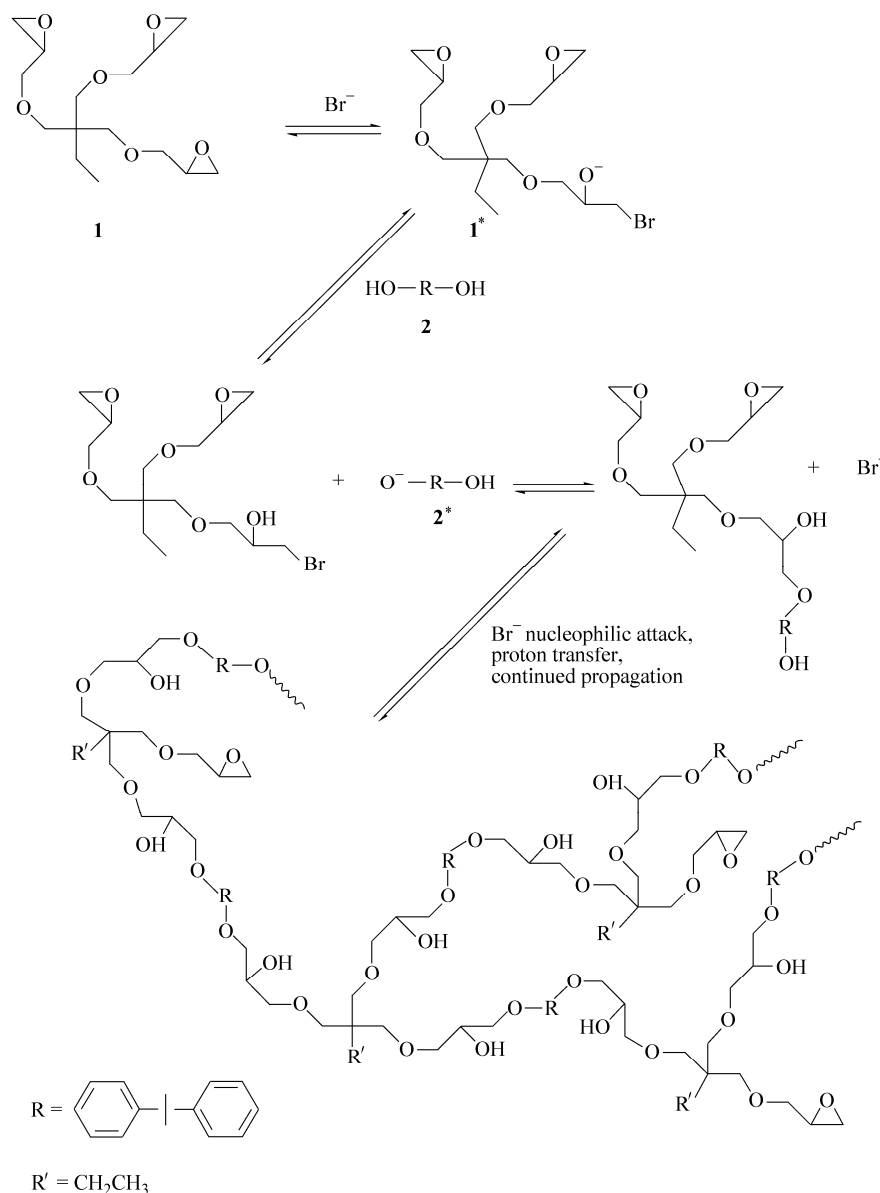
Synthesis of EHBP

The synthesis route and the ideal molecular structure of EHBP are shown in Scheme 1. Bu_4NBr was chosen to be the catalyst because the bromide ion, rather than hydroxide ion, was proved effective for controlling the polymerization to avoid cross-linking^[10, 17]. The reaction mechanism of proton transfer polymerization has already been described by Fréchet and coworkers^[7–11]. In this case, the polymerization mechanistic basis lies in the large disparity of the pK_a values of phenol and secondary alcohol as well as the different nucleophilicities of their corresponding anions. Also, there is the equilibrium between the epoxide ring opening by bromide ion and the base-induced ring closure of the resulting bromohydrin. In the late stages of polymerization, the depletion of the phenolic part effectively terminates the proton transfer and the equilibrium is shifted towards the closure of the bromohydrin to form epoxide moiety.

The reaction conditions and results are summarized in Table 1. The molar ratio of monomers was fixed at 1:1 to ensure that the epoxide functionalities were the main terminal groups. It can be seen from Table 1 that the reaction rate depends heavily on the reaction time (samples 1, 2 versus 3) with M_w increasing with time. It was found that when the reaction time was less than 20 h, the final mixture of THF solution and methanol was homogeneous, and no precipitation appeared. The reason could be that the $-\text{OH}$ groups in the synthesized hyperbranched polymers endow them with good solubility in methanol, especially for the low molecular weight oligomers. This can also be explained by the relatively low yield, the low molecular weight products were dissolved in methanol. The time dependence of the reaction is in correspondence with the step-growth polyaddition mechanism of this kind of reaction, in which the molecular weight growth is slow at the early stage (formation of low molecular oligomer) and gets faster at the later stage (coupling of oligomers). Gelation in the system of proton transfer polymerization can be easily avoided by removing reaction vessel from heating bath prior to gelation or lowering the temperature of reaction^[7]. This reaction proceeded homogeneously, and no gel formation was observed throughout the course of polymerization.

Table 1. Reaction conditions and results of polymerization

Entry	Time (h)	Temperature (°C)	Concentration (mol/L)	Initiator (mol% B3)	M_w	PDI	Yield (%)	T_g (°C)	Epoxide values (mmol/g)
1	22.5	68	1	5	8452	1.66	70	17.0	2.3
2	50	68	1	5	53370	2.16	72	21.9	2.0
3	90	68	1	5	87199	2.99	68	33.0	1.8
4	50	68	0.8	5	32990	2.10	67	20.0	2.1
5	90	60	1	5	57915	2.35	68	26.6	2.0
6	22.5	68	1	3	6619	1.64	69	15.0	2.4

**Scheme 1** Schematic outline for the synthesis of EHBP

As expected, the polymerization was accelerated with the elevated temperature (sample 3 versus sample 5 in Table 1). Because of the low boiling point of THF, the solvent used in the system, the increase of the reaction temperature is limited. However, it was found that the mild temperature, 68°C, was enough to afford rapid polymerization to produce high molecular weight products. Monomer concentration (sample 2 versus sample 4) and the amount of the initiator (sample 1 versus sample 6) also affected the polymerization. Higher amount of monomers and initiators facilitate chain growth which suggests that chain growth comes from the intermolecular reaction.

Structural Characterization

The structures of the resulting polymers were analyzed by $^1\text{H-NMR}$ and FT-IR spectroscopy, and the corresponding spectra of E20 were determined for comparison.

Figure 1 represents the ^1H -NMR spectra of EHBP and E20. Two similar spectra were observed. The two signals at $\delta = 0.77$ and 1.28 appear only in the spectrum of EHBP can be attributed to protons of methyl and methylene from TMPTG. The singlets at $\delta = 1.54$ of the spectra of EHBP and E20 are attributed to the methyl protons that are between the two benzene rings of BPA. The characteristic absorption due to epoxy groups are observed at $\delta = 2.51, 2.63$, and 3.00 in the spectrum of EHBP, and at $\delta = 2.60, 2.72$, and 3.20 in the spectrum of E20. The downfield of these three peaks in E20 to higher parts per million can be contributed to the decreased electron density around epoxy groups because of the electron-withdrawing ability of benzene adjacent to epoxy moieties. The broad multiplets at $\delta = 3.262\text{--}3.899$ in the two spectra are assigned to the methylene and methine protons adjacent to oxygen of ether and hydroxy moieties. The more complex nature of this part of EHBP spectrum shows its complex chemical structure due to uncontrolled branching. Hydroxyl protons give signals at $\delta = 4.96$ in EHBP spectrum, while at $\delta = 5.20$ in E20 spectrum. The doublets at $\delta = 6.31$ and 7.01 in the spectra of EHBP and E20 correspond to the aromatic protons.

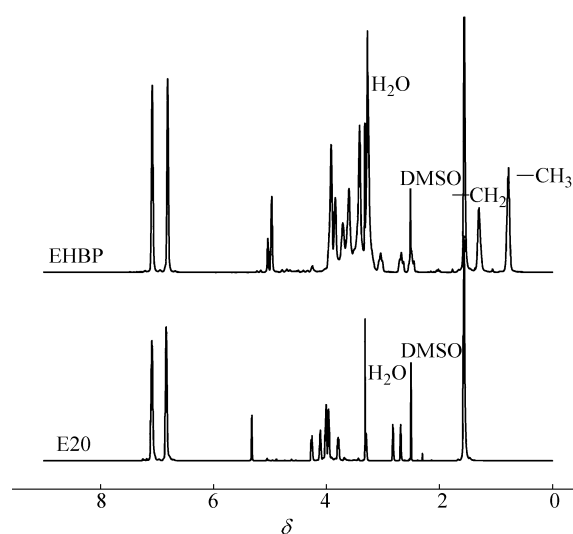


Fig. 1 ^1H -NMR spectra (DMSO- d_6 as solvent) of sample 1 (in Table 1) and E20

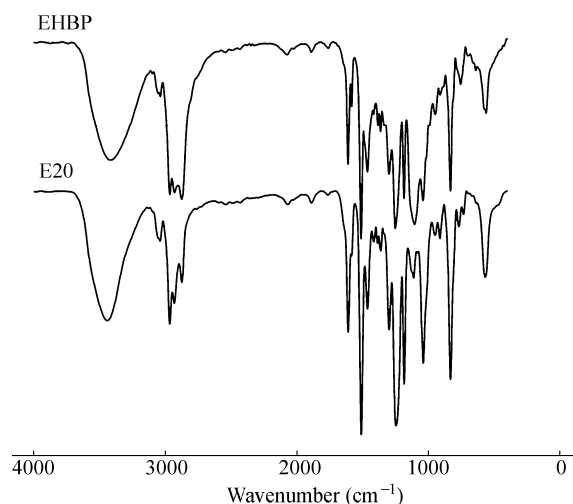


Fig. 2 FT-IR spectra of EHBP and E20

The FT-IR spectra of EHBP and E20 are presented in Fig. 2. Two almost similar spectra were observed again. FT-IR provides a rapid means of identifying functional groups. From the spectra of EHBP and E20, it is evident that the broad strong absorption around 3500 cm^{-1} corresponds to O—H stretching. The peaks at $2945\text{--}2870\text{ cm}^{-1}$ correspond to aliphatic (—C—H) stretching. The characteristic aromatic ring stretching is seen in both spectra at $1633\text{--}1515\text{ cm}^{-1}$. The peaks at $1248\text{--}1184\text{ cm}^{-1}$ and $1075\text{--}1010\text{ cm}^{-1}$ are assigned to asymmetrical and symmetrical stretching of =C—O—C and —C—O—C, respectively. The peaks at 908 cm^{-1} and 854 cm^{-1} indicate the presence of epoxy groups. The absorption due to Ph—H distorting appears at 820 cm^{-1} .

The similar spectra of ^1H -NMR and FT-IR clearly indicate the prepared EHBP is close to E20 structurally.

Thermal Properties

The thermal properties of the resulting EHBPs were studied using DSC and TGA. The midpoint of the slope change of the heating capacity plot in the DSC thermogram was taken as T_g . The analysis was first measured at a heating rate of 10 K/min . However, at this heating rate, the glass transition could not be clearly assigned. When the heating rate was increased to 20 K/min , the T_g could be clearly detected, as shown in Fig. 3. Similar increase in heating rate was also used in the literature^[19], in which the heating rate was increased from 10 K/min to 80 K/min to obtain a distinct T_g . In our work, the T_g values of the final polymers were in the range of 15°C to 33°C . The results are listed in Table 1. The M_{ws} of EHBPs had a significant effect on their thermal behaviors. The polymers with higher M_{ws} had higher T_g values. This can be attributed to the greater number of rigid aromatic rings and polar —OH groups in the backbone of products with higher M_{ws} . Moreover, the more highly branched molecular architecture of high M_w products reduces the mobility of the chain segments, leading to the increase of T_g values^[20]. Hyperbranched polymers with higher T_g values compared to their linear analogues have been reported^[21, 22].

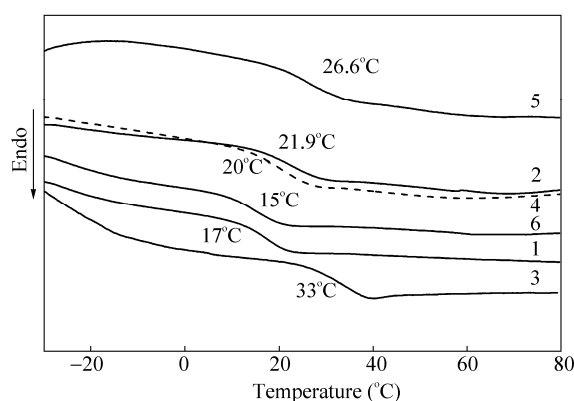


Fig. 3 DSC thermograms of EHBPs (numbering each curve according to Table 1)

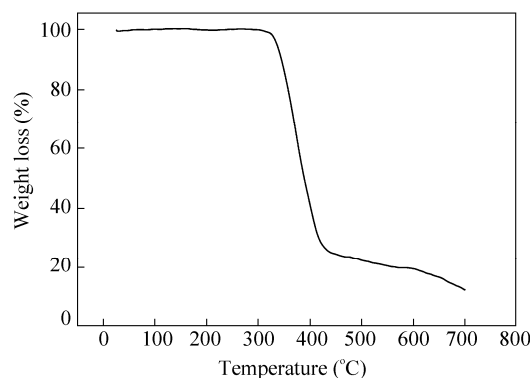


Fig. 4 Representative thermogravimetric analysis curve of EHBPs heated under nitrogen (scan rate 10 K/min)

TGA measurements revealed that EHBP had good thermal stability. A representative TGA curve of EHBP measured under nitrogen atmosphere is shown in Fig. 4, in which, a clearly two-step decomposition profile was observed. Fast decomposition occurred between 338°C and 414°C, and 74% weight loss was observed during the process. This may be explained by the breaking-down of abundant $-\text{OH}$ and $\text{C}-\text{O}-\text{C}$ groups in the molecule. After that, decomposition became slowly, and there was 12.47% residues remaining at 700°C corresponding to the stable $\text{C}-\text{C}$ bonds and aromatic rings in the structure.

Solubility and Solution Viscosities

The obtained EHBP had good solubility in polar solvents, such as THF, DMSO, CHCl_3 , acetone and poor solubility in low polar solvents like diethylether and benzene. This can be attributed to the existence of manifold of polar $-\text{OH}$ and $-\text{O}-$ groups, conferring great polarity to EHBP.

The viscosity of a given resin is considered as one of important processing parameters, as it affects flow ability, air release rate and curing rate, as well as the final properties of the cured film. Although products prepared in this work are in solid state, they show good solubility in acetone. Furthermore, they have good thinning ability with the addition of acetone, even for products with very high molecular weights. Sample 2 with M_w as high as 53370 was used to study this behavior and compared with E20 with molecular weight only near to 1000. The results are shown in Fig. 5. It can be seen that the viscosity of the EHBP acetone solution was not very high in spite of its high molecular weight. At 23 wt% loading of acetone, the solution viscosity of EHBP was 90.34 Pa·s, just slightly above the solution viscosity of E20, 77.75 Pa·s. The viscosity of EHBP acetone solution decreased more rapidly than that of E20 acetone solution. When the solutions were diluted to 40 wt% acetone, the two samples achieved nearly equal solution viscosity. The solution behavior reflects the highly branched nature of the prepared polymer, which makes them suitable for using as coating resin with proper solution viscosity and leveling ability even at elevated molar masses. This also means that less amount of organic solvents is enough to meet the demand of application. It is important because legislation has increasingly promoted the systems with lower volatile organic compounds (VOCs).

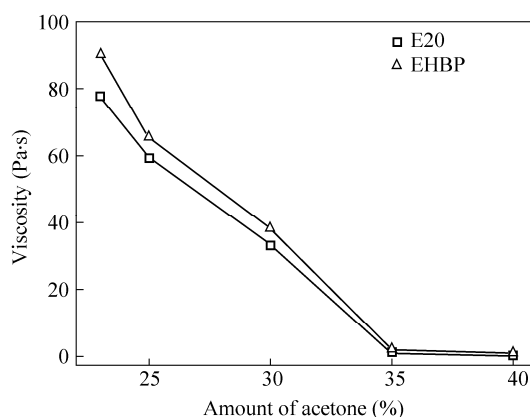


Fig. 5 Viscosities of acetone solutions of EHBP (sample 2 in Table 1) and E20

Curing and Film Properties

In order to compare the curing behavior and film properties, both E20 and the prepared EHBP containing 2.0 mmol epoxide per gram of resin determined by titration were cured with NX-2041. The results are summarized in Table 2. The thickness of the coatings was found to be around 70 μm .

It can be seen from Table 2, a faster cure-speed was observed for EHBP. The large amounts of epoxy substituents, which are mostly positioned at the periphery of EHBP and are readily accessible for the curing agent, contribute to the result. Films from EHBP/NX-2041 had better impact resistance and parallel hardness and adhesion compared with films based on E20/NX-2041. Similar structures, both of EHBP and E20 having multiple polar $-\text{O}-$ and $-\text{OH}$ groups and rigid aromatic bis-phenol structure, contribute to the equal

favorable properties comprising hardness and good adhesion to the metal substrate. The EHBP film showed better impact resistance than that based on E20, 120 cm versus 90 cm, mainly due to the relatively lower T_g value and longer flexible aliphatic spacers between rigid bisphenol A of EHBP. Impact resistance ability is particularly important for epoxy thermosets whose conventional forms are usually brittle and fragile in nature. By increasing the toughening properties of the cured resins, they may be used in broader applications.

As can be seen from Table 2, EHBP film showed higher gloss value than E20 film. The gloss values attest, in certain way, the smoothness of the paint surface. The paint films that exhibit high gloss have a smooth surface^[23]. Gloss property proves that EHBP had high leveling ability due to its compact structure leading to decreased inter-molecular interactions.

Table 2. Properties of the coating films based on sample 2 (in Table 1) and E20

Resins	Hand dry time (h)	Hard dry time (h)	Impact resistance (cm)	Pencil hardness (H)	Adhesion (grade)	Gloss (at 60°)
EHBP	1.5	12	120	3	1	102
E20	2.5	15	90	3	1	90

CONCLUSIONS

Hyperbranched counterparts of bisphenol-A type epoxy resin with a broad range of molecular weights and narrow molecular weight distributions were successfully prepared by proton-transfer polymerization of BPA and TMPTG at mild conditions. Their abilities to function as coating resins had been established through solution behavior, thermal properties and actual coating application, and improved properties were observed compared to those of bisphenol-A type epoxy resin.

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