



Facile synthesis toward self-dispersible waterborne comb-like Poly (hydroxyaminoethers)

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ABSTRACT

Water-dispersible polymers represent an evolved category in the chemical industry in terms of an eco-friendly technology to meet the desired performance and to reduce the use of volatile solvents. One of the major challenges in the development of water dispersible resins deeply relies on the emulsification process that often requires the ionization process or the use of additional surfactants. In this study, an efficient method for the preparation of amphiphilic comb-like poly(hydroxyaminoethers), which consists of hydrophobic epoxy resins as the backbone and hydrophilic polyethers as the side chains, were realized in the absence of catalysts or initiators. Different from the conventional epoxy resin dispersions prepared in the presence of surfactants, or through ionization process, these amphiphilic comb-like polymers exhibited self-dispersed properties to achieve stable non-ionic emulsions in the water. The hydrophilic contents of these comb-like poly(hydroxyaminoethers) could be easily tailored in a wide range from less than 20 wt% to over 65 wt%, along with glass transition temperatures ranged from $-45\text{ }^{\circ}\text{C}$ to $\sim 50\text{ }^{\circ}\text{C}$. In addition, the emulsifying ability was facilitated via the variations of the polymer architectures and compositions. Anti-corrosion properties were also evaluated for these self-dispersible poly(hydroxyaminoether) emulsions.

1. Introduction

The comb-like polymers are special type grafted polymers, which are regulated by the polymeric main chains and side chains alternatively [1–4]. Due to the incompatibility between the main chains and side groups, recent developments of amphiphilic block and graft copolymers consisting of hydrophilic and hydrophobic parts have drawn much attention [5]. Interesting phase transitions behavior as well as special performance materials for metallic ion complexation [6], stimuli-responsiveness [7] and emulsifying ability [8], are the basis for the success of advanced technologies such as solid polymer electrolytes [9,10], anti-fouling coatings [11], polymer blends [12], or adhesion/detachment substrates for cell culture [13].

Because of the above-mentioned unique properties and performances, the continuous effort on the synthetic methodology in the manipulation of the functionality, the sequence of main chain, the

length of side groups, the grafting degree, and the hydrophilic-lipophilic balance of comb-like polymers, holds promise to meet the increasing demand of new applications [14–16]. For example, Saunders et al. [17] reported an environmental responsive comb-like copolymer consisting of poly(*N*-isopropylacrylamide) (poly(NIPAM)) as the backbone, and poly(ethylene glycol) methacrylate as the side chains. This polymerization was proceeded by using 2,2'-azobis(2-methylpropionitrile) (AIBN) as initiator in the tert-butyl alcohol as solvents. As compared to the short-chain surfactants, these macro surfactants based on comb-like copolymers exhibited lower critical solution temperature. Georgiou et al. [8] developed a series of non-ionic comb-like polymeric macro-surfactants via group transfer polymerization. Unlike the typical emulsions prepared from the use of low molecular weight surfactants, these amphiphilic block copolymers consisting of the hydrophobic *n*-hexyl methacrylate and the hydrophilic poly(ethylene glycol) methacrylate would afford a series of stable emulsions.

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Polymer emulsions in aqueous solution have been developed in past few decades for both economic and environmental reasons. The specific polymer structure characteristics of hydrophilic units, as well as the use of surface active agents, determine the emulsion performance and properties [18]. As a result, polymer emulsions usually contain the surface active agents including ionic or non-ionic surfactants to provide stable emulsion stability. Furthermore, the introduction of hydrated functional groups such as carboxylic acids would be able to overcome the interactions between polymer and water after the ionization process [19]. The prominence of the polymer emulsions arises from the tailored-made performance in order to meet the requirements from advanced applications such as tissue engineering [20], nanowire aerogels [21], and conductive polymer binders [22].

This work is aiming to develop a feasible methodology for the preparation of self-dispersible comb-like amphiphiles without the need of catalysts or initiators. By using the commercially available epoxy resins and polyether amines, polymer structure-properties such as linear type and comb-like polymers with a wide range of glass transition temperatures (T_g s), and various degrees of self-dispersibility were made available. Unlike the traditional water dispersible epoxy polymers which are usually realized in the presence of additional surfactants [23–25] or proceeded via ionization process [26], these poly(hydroxyaminoethers) grounded by the comb-like architectures would exhibit self-dispersible ability, suitable for coating and anti-corrosion uses.

2. Results and discussion

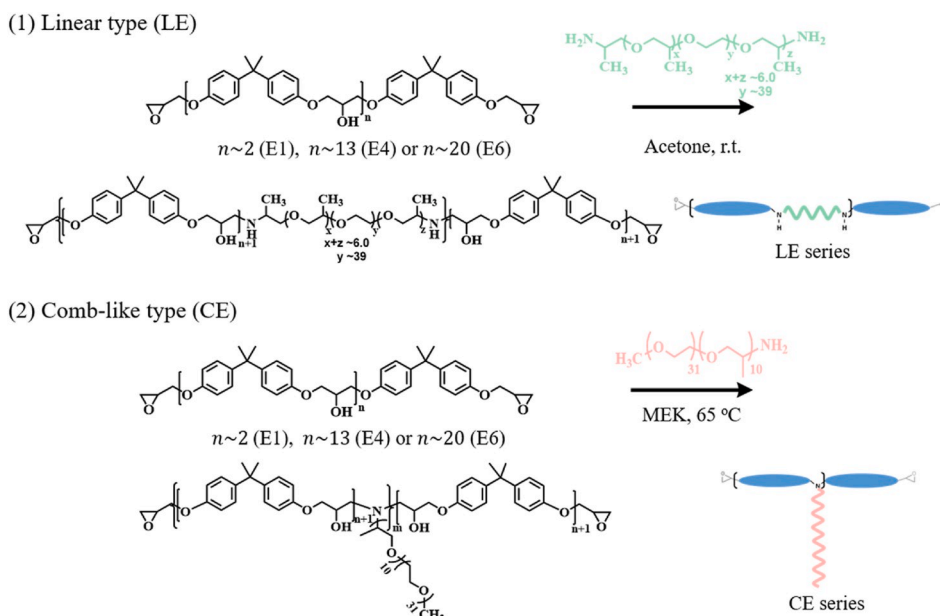
2.1. Synthesis and characterizations

The representative structures of the starting epoxides/amines and poly(hydroxyaminoethers) with linear and comb-like architectures are described in Scheme 1. The polymerizations were accomplished by the reaction between epoxide groups of the diglycidyl ether of bisphenol A (DGEBA) based epoxy resins, and the amino groups of the long-chain polyetheramines (Jeffamine® ED-2003 or M-2070). It is important to note that two possible reactions including the primary amine-epoxide and secondary amine-epoxide would be proceeded in the absence of catalyst [27]. Since the rate of epoxide reaction with the primary amine is more reactive than that with the secondary amine, this reaction was kept at room temperature to prevent the secondary amine-epoxy reaction until the extent of reaction was over 90% based on the given

stoichiometric functional groups as monitored by ^1H NMR spectra [28]. With this in mind, several sequences of poly(hydroxyaminoethers) with well-defined structures were investigated through the choice of DGEBA based epoxy resins with number average molecular weights ~ 1000 , ~ 4000 , and ~ 6000 , which are denoted as E1, E4, and E6, respectively. The water-soluble polyetheramine with the structure of poly(oxypropylene–oxyethylene–oxyethylene)bis(2-aminopropyl ether) (Jeffamine® ED-2003; 2000 g/mol) was utilized to react with E1, E4 and E6, respectively, to obtain three sequences of linear type poly(hydroxyaminoethers), namely E1-based sample (LE1), E4-based sample (LE4) and E6-based sample (LE6). In fact, poly(hydroxyaminoethers) with various theoretical number average molecular weights (M_n s) can be achieved through the reactions between epoxide and amino groups in different stoichiometric ratios. Three sequences composed of poly(hydroxyaminoethers) with theoretical M_n s such as ~ 10 k, ~ 20 k, ~ 30 k and >30 k (g/mol) are denoted as LE1-n, LE4-n, and LE6-n, where the “n” represents M_n , “1” is for ~ 10 k, “2” for ~ 20 k, “3” for ~ 30 k and “4” for >30 k (g/mol) (Table 1).

In the preparation of comb-like poly(hydroxyaminoethers), the polymerizations were also accomplished by the reaction between the epoxide functional groups on the DGEBA based epoxy resins, and mono amines of a water-soluble polyetheramine (Jeffamine® M-2070) as shown in Scheme 1. Since this polymerization would proceed the reactions first through primary amine-epoxide and then secondary amine-epoxide to achieve the tertiary amine as the branching point, these reactions were subjected to a higher temperature (80°C) than the polymerization temperature for the linear type poly(hydroxyaminoethers) mentioned earlier. The water-soluble polyetheramine with the structure of methoxy poly(oxyethylene–oxypropylene)-2-propylamine (Jeffamine® M-2070; 2000 g/mol) was utilized to react with E1, E4 or E6 in different stoichiometric ratios to obtain three sequences of comb-like poly(hydroxyaminoethers), such as E1-based sample (CE1), E4-based sample (CE4) and E6-based sample (CE6). Three sequences composed of poly(hydroxyaminoethers) with theoretical M_n s such as ~ 10 k, ~ 20 k, ~ 30 k and >30 k (g/mol) are denoted as CE1-n, CE4-n, and CE6-n, where the “n” represents M_n , “1” is for ~ 10 k, “2” for ~ 20 k, “3” for ~ 30 k and “4” for >30 k (g/mol) (Table 1).

The polymerization processes were monitored by using IR spectra as shown in Fig. 1. After polymerization, the disappearance of epoxide absorption peak at 913 cm^{-1} , and a newly emerged absorption peak of the C–N group at 1112 cm^{-1} were observed, indicating the completion



Scheme 1. Poly(hydroxyaminoethers) Prepared from Epoxy Resins with Polyetheramines for (1) Linear type, and (2) Comb-like Architectures.

Table 1
Formulations, compositions, and properties of Poly(hydroxyaminoethers).

Sample	Epoxy resin(mol)			Jeffamine®(mol)		J% ^{d)}	M _{n,cal.} ^{e)} (g/mol)	Thermal properties		Emulsion properties	
	E1 ^{a)}	E4 ^{b)}	E6 ^{c)}	ED-2003	M-2070			T _{d5} (°C)	T _g (°C)	Size ^{f)} (μm)	PDI
LE1											
LE1-1	5	–	–	4	–	61.5	13,000	316	–36	N.A.	N.A.
LE1-2	8	–	–	7	–	63.6	22,000	318	–39	N.A.	N.A.
LE1-3	12	–	–	11	–	64.7	34,000	319	–41	N.A.	N.A.
LE1-4	1	–	–	1	–	66.7	>34,000	321	–45	N.A.	N.A.
LE4											
LE4-1	–	3	–	2	–	25.0	16,000	334	22	N.A.	N.A.
LE4-2	–	4	–	3	–	27.3	22,000	330	18	N.A.	N.A.
LE4-3	–	6	–	5	–	29.4	34,000	331	12	N.A.	N.A.
LE4-4	–	1	–	1	–	33.3	>34,000	330	6	N.A.	N.A.
LE6											
LE6-1	–	–	2	1	–	14.3	14,000	345	47	N.A.	N.A.
LE6-2	–	–	3	2	–	18.2	22,000	337	37	N.A.	N.A.
LE6-3	–	–	4	3	–	20.0	30,000	338	31	N.A.	N.A.
LE6-4	–	–	1	1	–	25.0	>30,000	334	21	N.A.	N.A.
CE1											
CE1-1	5	–	–	–	6	61.5	13,000	308	–43	0.41	0.224
CE1-2	8	–	–	–	11	63.6	22,000	315	–47	0.33	0.108
CE1-3	12	–	–	–	16	64.7	34,000	315	–45	0.13	0.026
CE1-4	1	–	–	–	1	66.7	>34,000	303	–47	0.14	0.055
CE4											
CE4-1	–	3	–	–	2	25.0	16,000	342	18	0.13	0.029
CE4-2	–	5	–	–	4	27.3	22,000	339	14	0.22	0.047
CE4-3	–	7	–	–	6	29.4	34,000	337	10	0.45	0.035
CE4-4	–	1	–	–	1	33.3	>34,000	336	–1	0.43	0.126
CE6											
CE6-1	–	–	2	–	1	14.3	14,000	347	47	N.A.	N.A.
CE6-2	–	–	3	–	2	18.2	22,000	344	35	N.A.	N.A.
CE6-3	–	–	4	–	3	20.0	30,000	346	30	1.30	0.182
CE6-4	–	–	1	–	1	25.0	>30,000	343	18	1.20	0.005

a) E1 is epoxy resin with M_n of ~1000 g/mol.

b) E4 is epoxy resin with M_n of ~4000 g/mol.

c) E6 is epoxy resin with M_n of ~6000 g/mol.

d) The weight ratio of Jeffamine® in the polymer.

e) Theoretical M_n.

f) Number averages particle size measured by DLS.

of the reaction between epoxide group and amino group. The chemical structures of linear type and comb-like poly(hydroxyaminoethers) were further confirmed by ¹H NMR spectra in the examples of LE6-1 (Fig. 2) and CE6-1 (Fig. 3), respectively. In the ¹H NMR spectra, the significant decrease of integral area at δ = 2.88 ppm of oxirane group indicates that the extent of reaction between epoxide and amino groups were confirmed to be over 90%. Furthermore, according to the ¹H NMR integration analyses of the ratios between the aromatic protons (δ = 6.81) and residual epoxide group (δ = 2.88), the calculated M_{n,s} are 11,051 g/mol for LE6-1 (Figs. 2) and 10,951 g/mol for CE6-1 (Fig. 3). These results corroborate the calculated molecular weights determined by the stoichiometric ratios between epoxide and amino groups.

2.2. Thermal properties

Thermogravimetric analysis (TGA) results of the poly(hydroxyaminoethers) are listed in Table 1. When the molecular weight of the polymer increased, the 5 wt % weight loss temperature (T_{d5}) increased slightly from LE1-1 (316 °C), LE1-2 (318 °C), LE1-3 (319 °C), to LE1-4 (321 °C). When the starting epoxy materials changing from E1 (M_n ~ 1000 g/mol) to E4 (M_n ~ 4000 g/mol) or E6 (M_n ~ 6000 g/mol), the LE4 series (LE4-1 (334 °C), LE4-2 (330 °C), LE4-3 (331 °C), and LE4-4 (330 °C)) exhibited similar T_{d5} temperatures to those of LE6 series (LE6-1 (345 °C), LE6-2 (337 °C), LE6-3 (338 °C), and LE6-4 (334 °C)).

Furthermore, the comb-like poly(hydroxyaminoethers) (CE1-1 (308 °C), CE1-2 (315 °C), CE1-3 (315 °C), and CE1-4 (303 °C); CE4-1 (342 °C), CE4-2 (339 °C), CE4-3 (337 °C), and CE4-4 (336 °C); CE6-1 (347 °C), CE6-2 (344 °C), CE6-3 (346 °C), to CE6-4 (343 °C)) also exhibited similar T_{d5} temperatures to those of their linear type analogues. It seems that the T_{d5} temperatures were mainly dependant on the polyetheramine content (J%; “J” derives from Jeffamine®, i.e., the percentage of Jeffamine® component in the poly(hydroxyaminoether), while independent on the sequences, molecular weights, or architectures of poly(hydroxyaminoethers). In summary, poly(hydroxyaminoethers) in this study exhibited good thermal stability over 300 °C.

Thermal phase transitions such as glass transition (T_g) and melting temperature (T_m) are shown in Figs. 4–6. During the second round heating, the disappearance of melting transitions from pristine polyetheramines (T_m ~38 °C for ED-2003 and T_m ~10 °C for M-2070, see Fig. 4) and the newly emerged glass transitions (T_gs) indicate that the presence of epoxy units prevented the crystallization and resulted in the amorphous state (Figs. 5 and 6). In addition, these newly emerged T_gs were shifted from the T_gs of pristine epoxy resins (T_g ~37.0 °C for E1, T_g ~59.8 °C for E4 and T_g ~83.0 °C for E6, see Fig. 4) to lower temperatures with increasing content of Jeffamine® since the T_gs of the polyetheramines are about –50 °C [29].

In addition to the formulation and composition factors, the T_gs also depended on the polymer architectures as shown in deviations between

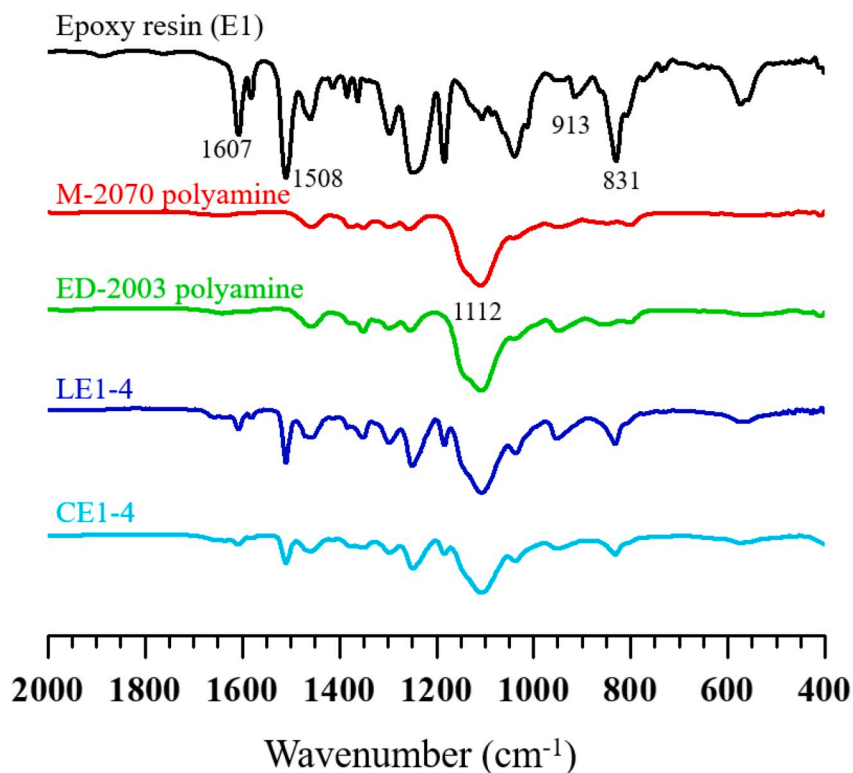


Fig. 1. IR spectra of linear type and comb-like Poly(hydroxyaminoethers).

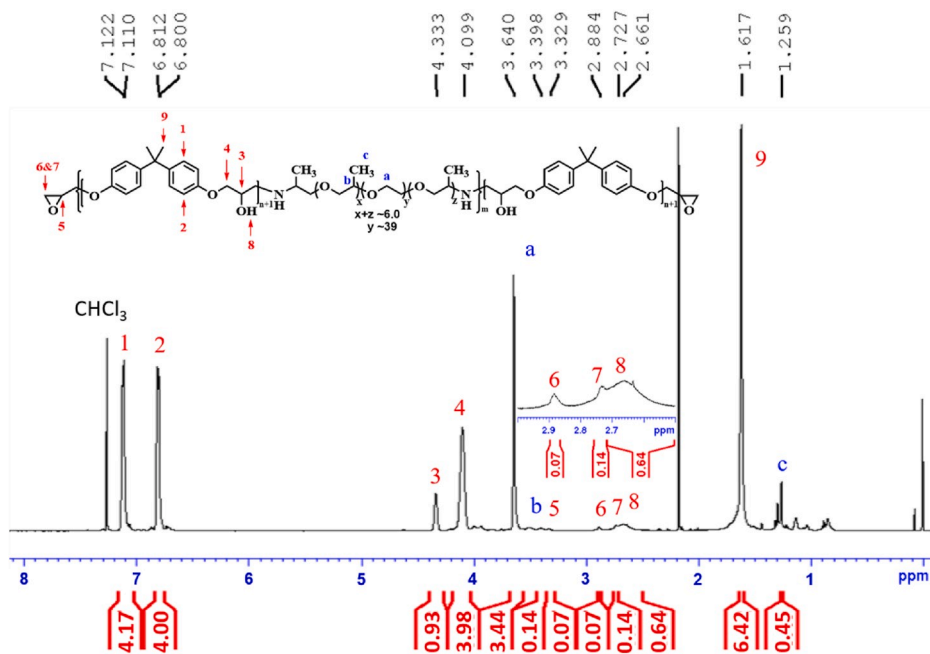


Fig. 2. ^1H NMR spectra of linear type Poly(hydroxyaminoethers) of LE6-1.

the T_g s measured by DSC [30–33], and the theoretical T_g s calculated by using the empirical Fox equations (Fig. 7). The T_g s of LE series were closer to the theoretical T_g s than those of the CE series were due to the incorporation of more branching points in the CE series [34].

2.3. Polymer dispersion and application

Following the emulsification process, these poly

(hydroxyaminoethers) were dispersed into water in one-pot to prepare waterborne polymer dispersions. The emulsion properties are shown in Table 1. Unlike the linear type analogues, most of the comb-like poly (hydroxyaminoethers) (CE series), except CE6-3 and CE6-4 comprising less than 20% of hydrophilic polyetheramine, were able to be self-dispersed in the water. This is because the freer hydrophilic side chains of the CE series swelled better in water and provided better dispersion capability than did the restrained hydrophilic chains between

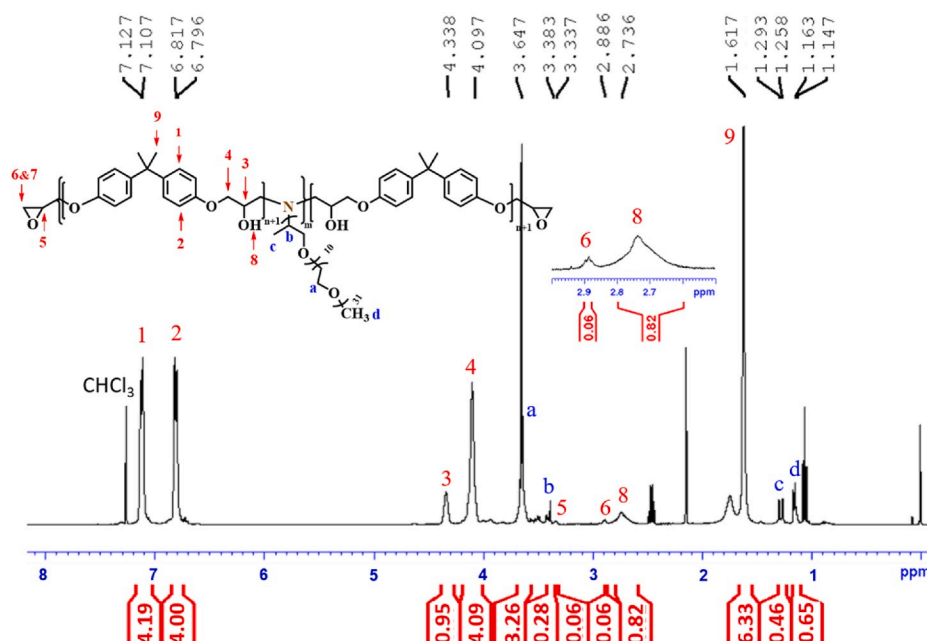


Fig. 3. ^1H NMR spectra of comb-like Poly(hydroxyaminoethers) of CE6-1.

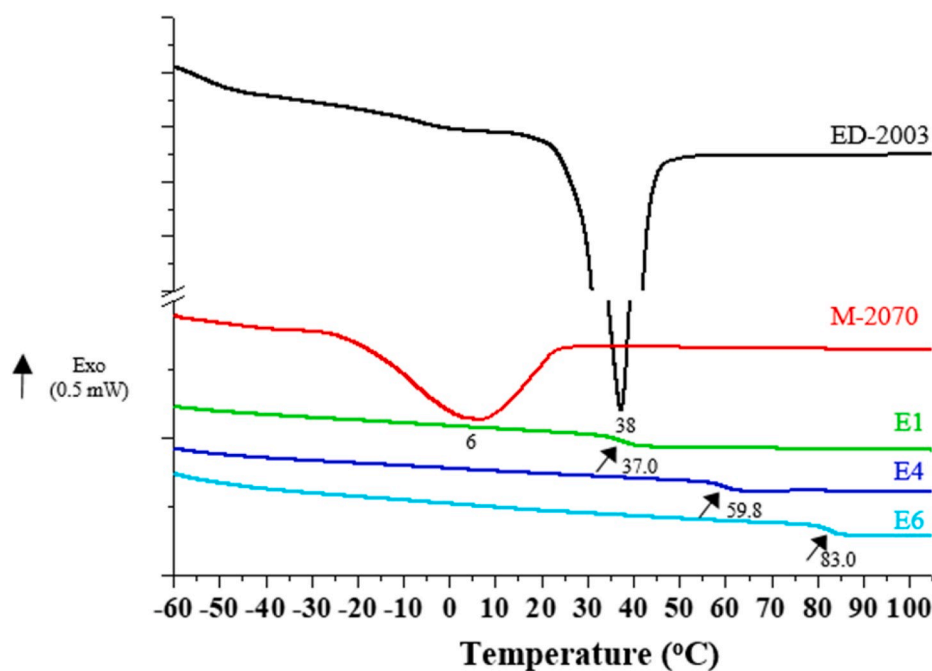


Fig. 4. DSC Thermograms of DGEBA based epoxy resins, and polyetheramines.

epoxy blocks in LE series [8]. Consequently, the comb-like poly (hydroxyaminoethers) presented satisfactory emulsifying ability to achieve stable emulsions with sizes ranging from 0.13 μm to around 1.3 μm .

For CE1 series with the short hydrophobic epoxy chain length, the particle sizes were relatively small in average when compared to the other comb-like series due to the higher fraction of hydrophilic polyetheramine (J%). In addition, the particle size would decrease with increasing hydrophilicity (CE1-1 (0.41 μm), CE1-2 (0.33 μm), CE1-3 (0.13 μm) and CE1-4 (0.14 μm)). For CE4 series with a moderate hydrophobic epoxy chain length and a lower fraction of hydrophilic polyetheramine, the particle sizes were slightly larger than those of CE1

series. However, in contrast to CE1 series, the particle size was increased with increasing hydrophilicity for CE4 series. This could possibly be attributed to the softness of the particles [35]. As shown in Table 1, the T_g of CE4 series was significantly reduced from 18 to -1 $^{\circ}\text{C}$ as the content of flexible polyetheramines was increased. In other words, the particles were greatly softened with increasing fraction of polyetheramines. It has been shown that soft particles tended to coalesce under the external shear force during the emulsification process [35]. The coalescence of the softer particles upon shearing may explain the phenomena observed here. For CE6 series with a longer hydrophobic epoxy chain length, more hydrophilic polyetheramines were required to form stable emulsions. CE6-1 and CE6-2 with low hydrophilic contents, 14.3

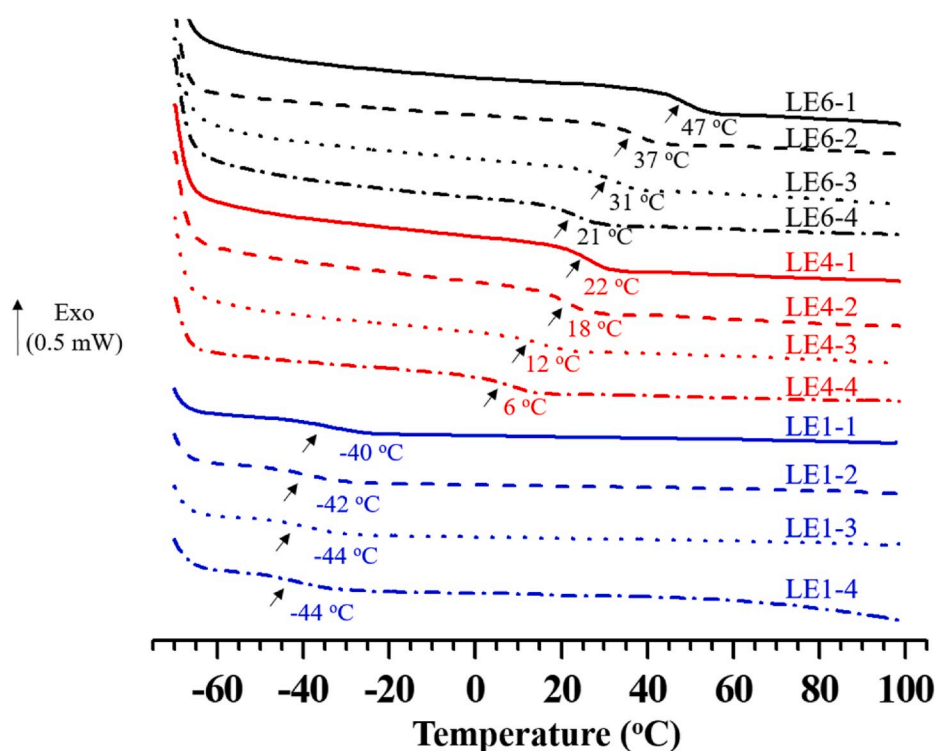


Fig. 5. DSC thermograms of linear Poly(hydroxyaminoethers).

and 18.2%, respectively, were unable to be emulsified because such a low fraction of the hydrophilic polyetheramines was insufficient to stabilize the hydrophobic epoxy content. CE6-3 and CE6-4 with relatively high hydrophilic contents, 20.0 and 25.0%, respectively, could be emulsified but with larger particle sizes. The emulsified CE6-4 sample exhibited a particle size of 1.2 μm , which is 10 times larger than that of the emulsified CE4-1 sample with the same 25.0% hydrophilic content

(0.13 μm). This is because the longer hydrophobic epoxy backbone would restrict the motion of flexible hydrophilic polyetheramine segments and thus lowered the emulsifying capability [36].

Further comparing the short-length comb-like polymers with molecular weights about 10,000 g/mol, CE1-1 and CE4-1 exhibited particle sizes of 0.41 μm (polydispersity (PDI) = 0.22), and 0.13 μm (PDI = 0.03), respectively, while CE6-1 was unable to form stable emulsions. It

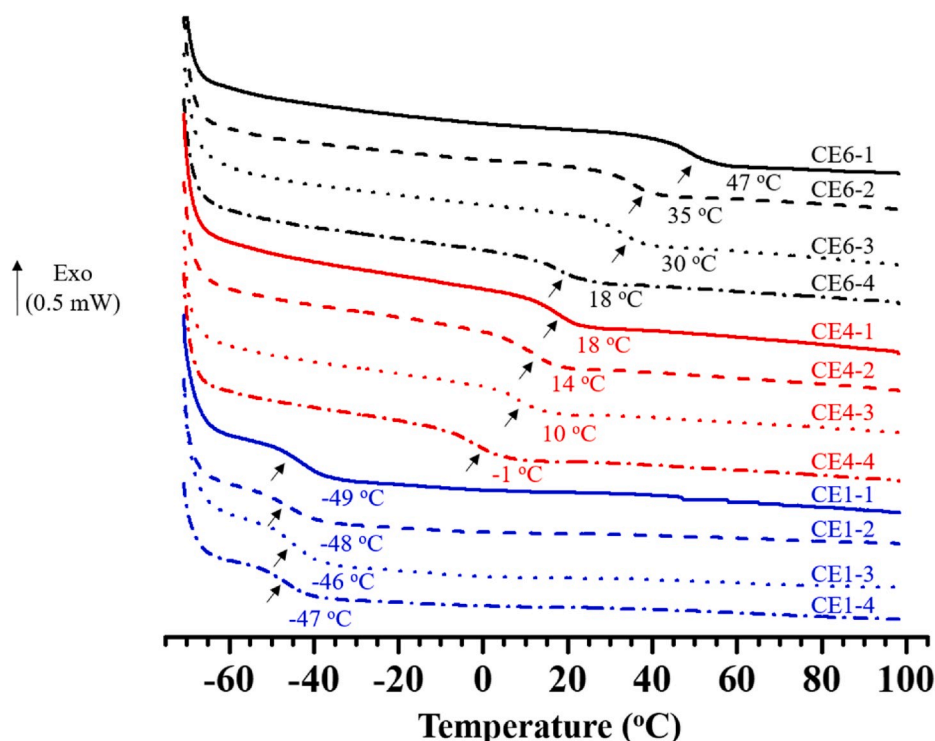


Fig. 6. DSC thermograms of comb-like Poly(hydroxyaminoethers).

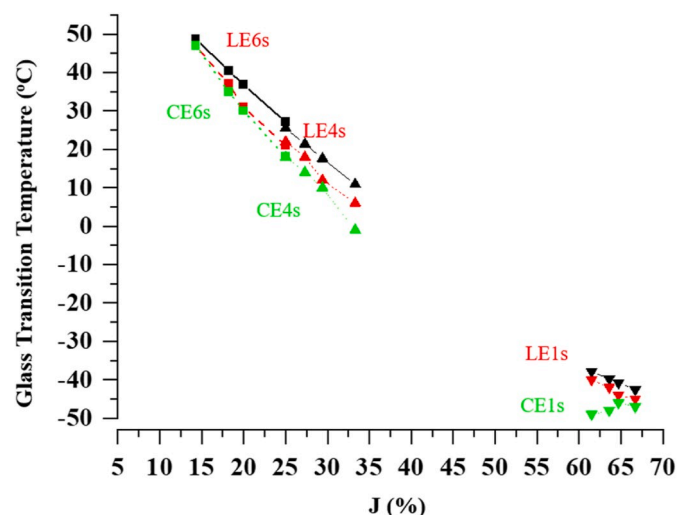
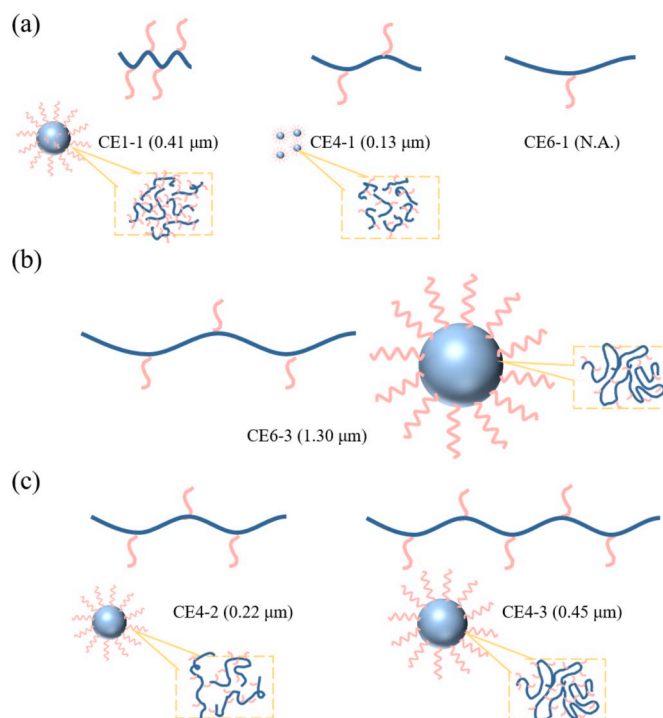


Fig. 7. Calculated T_g ($^{\circ}\text{C}$) by Using Fox Equation (red), Linear Type Poly(hydroxyaminoethers) (black) and Comb-like Poly(hydroxyaminoethers) (green) versus Polyetheramine contents (J%). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

is intriguing that the particle size of CE1-1 comprised 61.5% of the hydrophilic polyetheramines was larger than that of CE4-1 comprised only 25.0%. This is possibly also due to the much lower T_g of CE1-1 (-43°C) compared to that of CE4-1 (18°C). Along with the low molecular weights that are unable to form sufficient entanglements to lower the fluidity, the soft CE1-1 particles hardly maintained their shape and tended to coalesce under shearing, which thus caused a larger size as well as a larger PDI. With an optimal hydrophobic/hydrophilic ratio, the CE4-1 sample with a high T_g (18°C) was able to create stable dispersions in water with a smaller particle size and PDI. In contrast, CE6-1 was unable to be dispersed in water due to the low hydrophilicity.

Based on the different sequences of comb-like structures, various self-emulsifying performances were realized in the formation of different particle sizes as illustrated in Scheme 2. In summary, from the above emulsifying results, the emulsifiability and the particle size are determined by the following factors: the architecture of the poly(hydroxyaminoethers) that regulates the water solubility of the



Scheme 2. Illustrations of Particle Formation for Water Dispersed Poly(hydroxyaminoethers).

polyetheramine, the fraction of the hydrophilic content that provides the emulsifying capability (Scheme 2(a)), the length of the rigid hydrophobic epoxy that can restrict the flexible polyetheramine chain mobility (Scheme 2(b)), and the softness of the particles and the external shear force that may cause coalescence during the emulsification process (Scheme 2(c)).

These versatile self-dispersible poly(hydroxyaminoethers) were then proceed one example of the application on the anti-corrosion coating for steel sheets. In the corrosion test, the steel sheet samples were coated with poly(hydroxyaminoethers) emulsions and exposed to a corrosive environment with salt spray and fog for 24 h, according to the ASTM B117 standard (Fig. 8). For the sake of comparison, a non-self-

Sample	CE1-4	LE6-4+SDS	CE4-1	CE6-3
Glass transition temperature ($^{\circ}\text{C}$)	-47	21	18	30
Appearance after 24h corrosion test				

Fig. 8. Photographs of CE1-4, LE6-4 with 3 wt% SDS, CE4-1, and CE6-3 emulsions-coated steel sheets after 24 h of salt spray exposure according to ASTM B117.

dispersible sample, LE6-4 was emulsified with the assistance of 3 wt% anionic surfactants sodium dodecyl sulfate (SDS). For the CE1-4 sample, severe corrosion and yellowing were observed after 24 h exposure of the salt spray. This result was attributed to the low T_g of -47°C that allowed salt penetration onto the surface [37–39]. When the steel surface was coated with the small-molecule surfactant-containing LE6-4 emulsion with a higher T_g (20°C), the degree of anti-corrosion was much improved, yet many defects were still present. It is concluded that the utilization of ionic small molecule surfactant to prepare poly(hydroxyaminoether) emulsions did not reach the intended anti-corrosion performance. The steel surface was also coated with self-dispersible CE4-1 emulsion with a T_g of 18°C . It is important to note that the anti-corrosion effect was further improved to be defectless. Moreover, the steel sample coated with the self-dispersible CE6-3 emulsion comprising a relatively high T_g of 30°C also exhibited similar effectiveness in anti-corrosion.

3. Conclusion

In this work, a facile methodology for preparing non-ionic comb-like poly(hydroxyaminoether) emulsions was presented. The hydrophilic contents of polyetheramines and polymer architectures were tailored through a simple synthesis in the absence of catalysts under mild conditions. Unlike their linear type analogues, the comb-like poly(hydroxyaminoethers) were able to produce stable water dispersions due to the presence of the hydrophilic side chains. A wide range of dispersion products ranging from less than 20 wt% to over 65 wt% of polyetheramines contents were realized. These products are thermally stable at temperatures over 300°C , featuring tunable glass transitions ranging from -45°C to $\sim 50^\circ\text{C}$. With the incorporation of hydrophilic side chains, and optimized compositions, the comb-like poly(hydroxyaminoethers) of CE4-1 exhibited best water dispersible characteristics with a size of $0.13\ \mu\text{m}$ and a polydispersity as low as 0.029 without the need of using surfactants or ionization process. Most importantly, these comb-like poly(hydroxyaminoethers) were able to pass anti-corrosion tests on the steel surfaces according to ASTM B117.

4. Experimental section

4.1. Materials

DGEBA based epoxy resins such as BE-501 ($M_w \sim 1000$; E1), BE-507 ($M_w \sim 4000$; E4) and BE-509 ($M_w \sim 6000$; E6) were purchased from CCP group (Chang Chun Group, Taiwan). Jeffamine® ED-2003 ($M_w \sim 2000$) and M-2070 ($M_w \sim 2000$) were provided by Huntsman Corp. Solvents including acetone (Sigma-Aldrich) and methyl ethyl ketone (MEK; Sigma-Aldrich) were distilled under reduced pressure over MgSO_4 or CaH_2 and stored over $4\ \text{\AA}$ molecular sieves. Other reagents were used as received without further purification.

4.2. Instrumentations

Infrared (IR) spectra were recorded using a Jasco 4100 FT-IR Spectrophotometer with a Jasco ATR Pro 450-S accessory. ^1H NMR spectra were taken on a Bruker Avance-400 MHz FT-NMR spectrometer with chloroform-d or dimethyl sulfoxide- d_6 . Glass transition temperature (T_g), and melting temperature (T_m) were measured under a N_2 atmosphere using a differential scanning calorimeter (DSC, TA Instruments, TA-Q20) operated at a heating rate of $10^\circ\text{C}\ \text{min}^{-1}$. Thermogravimetric analysis (TGA) was carried out using a Q50 thermogravimetric analyzer (TA instruments) operated under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The average particle size and bimodal distribution were measured by dynamic light scattering (DLS) equipped with a particle size analyzer (90 Plus, Brookhaven Instrument Corp.) and a 15 mW solid-state laser ($\lambda = 675\ \text{nm}$). The corrosion tests were carried out by coating the polymer emulsions on the steel samples ($70 \times 150\ \text{mm}^2$)

under the salt spray cabinet according to the ASTM B117 standard [40, 41].

4.3. General procedure for preparation of Poly(hydroxyaminoethers)

4.3.1. Preparation of linear type poly(hydroxyaminoethers)

In a typical polymerization procedure, LE1-1 as an example, DGEBA based epoxy resin of E1 ($M_n \sim 1,000$, 25.0 g, 25 mmol) was dissolved in the 80 ml of MEK at 50°C in a 500 ml four necked flask equipped with a mechanical stirrer, reflux condenser, thermometer, and nitrogen inlet. Subsequently, a diluted solution of poly(oxypropylene–oxyethylene–oxyethylene)bis(2-aminopropyl ether) (Jeffamine® ED-2003, 40.0 g, 20 mmol in 10 ml acetone) was added dropwise with a rate of 1 drop/s into the epoxy resin solution. The reaction was kept at room temperature until the theoretical integral area ratio was over 90% as determined by the ^1H NMR spectra. ^1H NMR (400 MHz, $d\text{-CDCl}_3$): $\delta(\text{ppm}) = 1.25$ (d, $J = 20.15\ \text{Hz}$, 0.45H), 1.61 (s, 6.42H), 2.66 (m, 0.64H), 2.72 (m, 0.14H), 2.88 (s, 0.07H), 3.32 (s, 0.07H), 3.39 (s, 0.14H), 3.64 (s, 3.44H), 4.09 (s, 3.98H), 4.33 (s, 0.93H), 6.81 (d, $J = 7.66\ \text{Hz}$, 4.00H), 7.12 (d, $J = 8.02\ \text{Hz}$, 4.17H). FT-IR (KBr): $1508\ \text{cm}^{-1}$ and $1607\ \text{cm}^{-1}$ (p-sub. benzene ring quadrant stretching), $1112\ \text{cm}^{-1}$ (C–N stretching vibrations), absence of $913\ \text{cm}^{-1}$ (ring vibration of epoxy ring), $831\ \text{cm}^{-1}$ (1,4-substitution of aromatic ring).

Three sequences of linear type poly(hydroxyaminoethers) prepared by using various DGEBA based epoxy resins with M_n s ~ 1000 (E1), ~ 4000 (E4), or ~ 6000 (E6) to obtain E1-based samples (LE1), E4-based samples (LE4) or E6-based samples (LE6). Based on the above mentioned procedure, poly(hydroxyaminoethers) with various theoretical M_n s could also be achieved through the reactions between epoxide and amino groups in different stoichiometric ratios. In fact, linear type poly(hydroxyaminoether)s with theoretical M_n s such as $\sim 10\ \text{k}$ (LE1-1, LE4-1, LE6-1), $\sim 20\ \text{k}$ (LE1-2, LE4-2, LE6-2), $\sim 30\ \text{k}$ (LE1-3, LE4-3, LE6-3) and $>30\ \text{k}$ (g/mol) (LE1-4, LE4-4, LE6-4) were achieved. The polymerization was kept at room temperature to prevent the secondary amine-epoxy reaction until the extent of reaction was over 90% as monitored by ^1H NMR spectra. Formulations, compositions, and calculated molecular weights are compiled in Table 1.

4.3.2. Preparation of comb-like poly(hydroxyaminoethers)

In a typical polymerization procedure, CE1-1 as an example, epoxy resins E1 ($M_w \sim 1,000$, 25.0 g, 25 mmol) was dissolved in the 80 ml of MEK at 65°C in a 500 ml four necked flask equipped with a mechanical stirrer, reflux condenser, thermometer, and nitrogen inlet. Subsequently, a diluted solution of methoxy poly(oxyethylene–oxypropylene)-2-propylamine (Jeffamine® M – 2070, 40.0 g, 20 mmol in 10 ml MEK) was added dropwise with a rate of 1 drop/s into the epoxy resins solution. The reaction was kept at 80°C until the theoretical integral area ratio was over 90% as determined by the ^1H NMR spectra. ^1H NMR (400 MHz, $d\text{-CDCl}_3$): $\delta(\text{ppm}) = 1.15$ ppm (d, $J = 6.40\ \text{Hz}$, 0.65H), 1.25 (d, $J = 13.61\ \text{Hz}$, 0.46H), 1.61 (s, 6.33H), 2.72 (m,

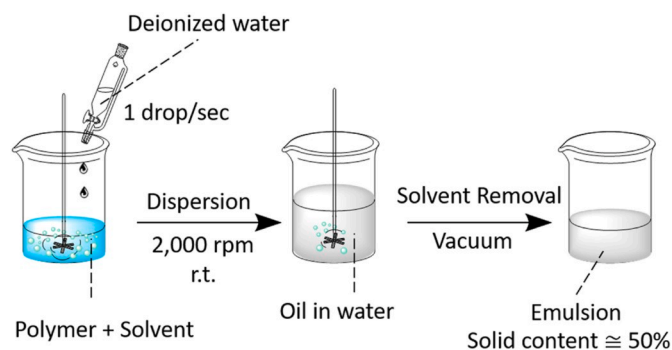


Fig. 9. Preparation of water dispersed Poly(hydroxyaminoethers).

0.82H), 2.88 (s, 0.06H), 3.32 (s, 0.06H), 3.39 (s, 0.28H), 3.64 (s, 3.26H), 4.09 (s, 4.09H), 4.33 (s, 0.95H), 6.81 (d, $J = 8.20$ Hz, 4.00H), 7.12 (d, $J = 8.63$ Hz, 4.19H). FT-IR (KBr): 1508 cm^{-1} and 1607 cm^{-1} (p-sub. benzene ring quadrant stretching), 1112 cm^{-1} (C–N stretching vibrations), absence of 913 cm^{-1} (ring vibration of epoxy ring), 831 cm^{-1} (1,4-substitution of aromatic ring).

Three sequences of comb-like poly(hydroxyaminoethers) prepared by using various DGEBA based epoxy resins with M_n s ~1000 (E1), ~4000 (E4), or ~6000 (E6) to obtain E1-based samples (CE1), E4-based samples (CE4) or E6-based samples (CE6). Based on the above mentioned procedure, poly(hydroxyaminoethers) with various theoretical M_n s could also be achieved through the reactions between epoxide and amino groups in different stoichiometric ratios. In fact, comb-like poly(hydroxyaminoether)s with theoretical M_n s such as ~10 k (CE1-1, CE4-1, CE6-1), ~20 k (CE1-2, CE4-2, CE6-2), ~30 k (CE1-3, CE4-3, CE6-3) and >30 k (g/mol) (CE1-4, CE4-4, CE6-4) were achieved. The polymerization was kept at 80 °C to assure the complete amine-epoxy reaction as monitored by ^1H NMR spectra. Formulations, compositions, and calculated molecular weights are compiled in Table 1.

4.4. General procedure for Water Dispersed Poly(hydroxyaminoethers)

The poly(hydroxyaminoethers) in MEK were directly dispersed by adding deionized water dropwise at room temperature under mechanical dispersion process at 2000 rpm (Fig. 9). A milk white poly(hydroxyaminoether) emulsion with 50% solid content was obtained after mixing poly(hydroxyaminoethers) and water thoroughly and stirring for additional 30 min, followed by subsequent removal of solvent. The particle size and polydispersity index (PDI) of polymer dispersions were measured by using dynamic light scattering (DLS) as shown in Table 1.

4.5. Theoretical molecular weight calculations for Poly(hydroxyaminoethers)

The polymerization in this study was carried out by using the reaction between amine and epoxy functional groups. The theoretical $M_{n,cal}$ of the stepwise polymerization was calculated according to the following formula by using the ratio of reactive functional group [42].

$$M_{n,cal} = M_{epoxy} n_{epoxy} + M_{Jeffamine} n_{Jeffamine}$$

M_{epoxy} is the molecular weight of epoxy resin;
 $M_{Jeffamine}$ is the molecular weight of Jeffamine®;
 n_{epoxy} is the mole number of epoxy resin;
 $n_{Jeffamine}$ is the mole number of Jeffamine®.

4.6. Theoretical glass transition calculations by using Fox equation [43]

The T_g s of poly(hydroxyaminoethers) are dependent on the initial T_g s of epoxy resins and polyetheramines. The theoretical T_g could be obtained by using a simple empirical formula that relates weight ratios to the T_g s of epoxy resins and polyetheramines as shown in the following:

$$\frac{1}{T_g} = \frac{\omega_{epoxy}}{T_{g,epoxy}} + \frac{\omega_{Jeffamine}}{T_{g,Jeffamine}}$$

ω_{epoxy} is the weight fractions of epoxy resin;
 $\omega_{Jeffamine}$ is the weight fractions of Jeffamine®;
 $T_{g,epoxy}$ is the glass transition temperature of pristine epoxy resin;
 $T_{g,Jeffamine}$ is the glass transition temperature of pristine Jeffamine®.

4.7. The preparation of anti-corrosion thin film on the steel sheet

To coat anti-corrosion thin film, the steel sheet was first wash with

detergents for three times to clean the steel surface. The water borne epoxy emulsion was then coated on the steel surface by using a rod-coating (Meyer rod) technique to obtain a uniform thin film with a thickness of about 5 μm [44,45]. After heating and drying at 200 °C in circulation oven for 5 min, the coating process of anti-corrosion thin film on the steel surface was completed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Chien-Hsin Wu: Conceptualization, Methodology, Software, Writing - original draft. **Ying-Chi Huang:** Data curation, Investigation. **Tai-Hong Lai:** Investigation, Data curation. **Sin-Huei Chiu:** Investigation. **Nishiki Uchibe:** Investigation. **Hsin-Wei Lin:** Conceptualization, Investigation. **Wen-Yen Chiu:** Supervision. **Shih-Huang Tung:** Writing - review & editing, Supervision. **Ru-Jong Jeng:** Writing - review & editing, Supervision.

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