Support information

The novel waterborne UV-curable coatings based on hyperbranched polymer via electrophoretic deposition

Junhua Chen [ac], Kaimei Peng [*b], Weiping Tu [*a]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China.

[b] School of Chemistry and Chemical Engineering, Qiannan Normal University for Nationalities, Duyun 558000, China

[c] School of Environmental and Chemical Engineering, Zhaoqing University, Zhaoqing 526061, China

*Corresponding Authors:

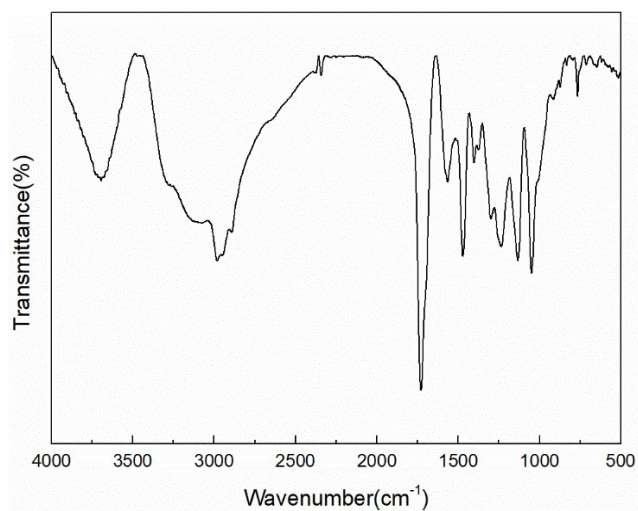E-mail: cewptu@yeah.net (W. Tu), scutpkm@163.com (K. Peng)
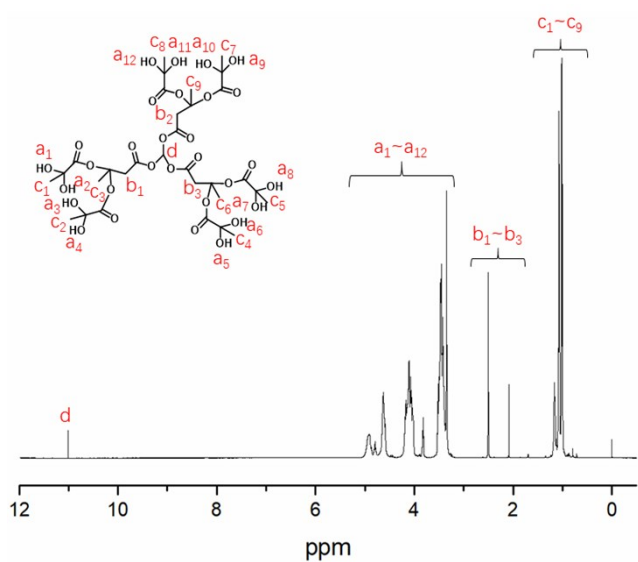
Fig. S1. FT-IR spectrum of H202
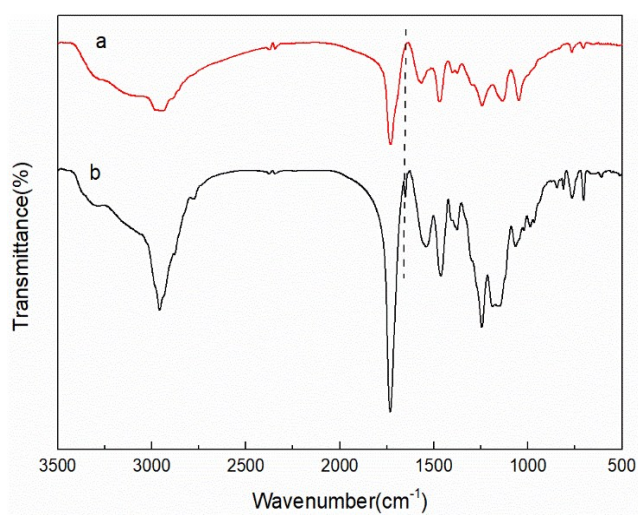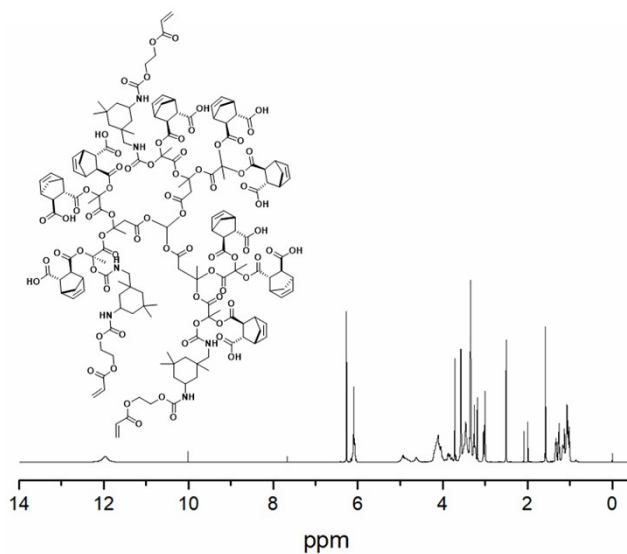

Fig. S2. ^{1}H-NMR spectrum of H202

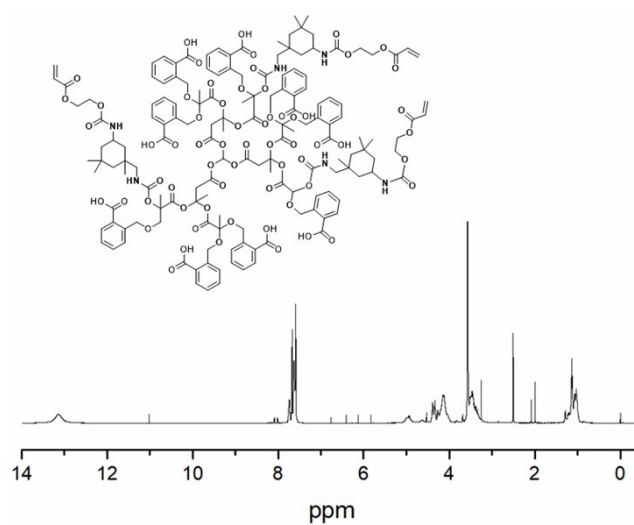**Fig. S4.** ^{1}H-NMR spectrum of HBPE-CDA-IPDI-HEA39

Fig. S5. ^{1}H-NMR spectrum of HBPE-PA-IPDI-HEA39
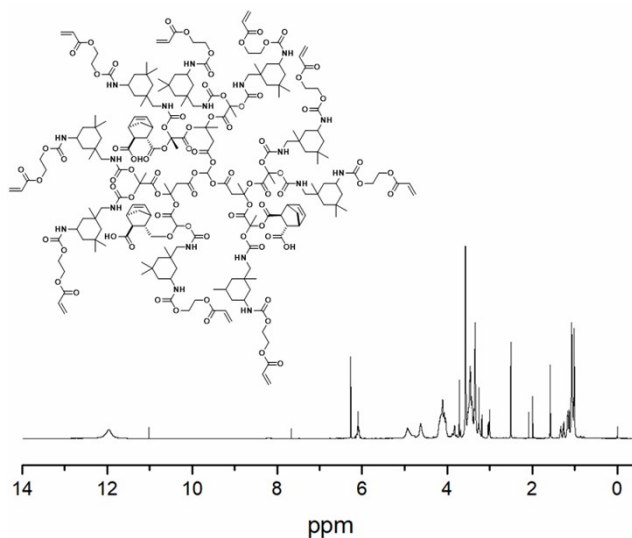
Fig. S6. ^{1}H-NMR spectrum of HBPE-CDA-IPDI-HEA93
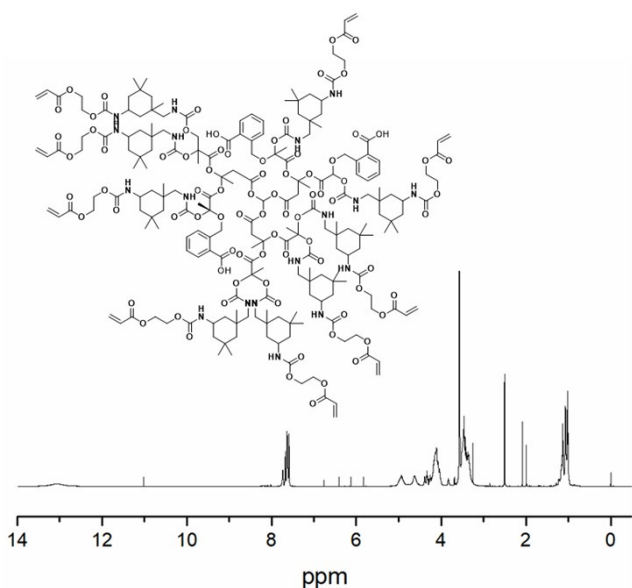
Fig. S7. ^{1}H-NMR spectrum of HBPE-PA-IPDI-HEA93

The size exclusion chromatography analysis conformed to narrowly dispersed polystyrene standards using tetrahydrofuran (THF) as the eluent. As shown in Fig. S8 and Table S1, the number average molecular weight Mn of unmodified WPA was measured to be ~10.185 kg/mol, and the polydispersity index Mw/Mn was 1.786. Based on the Mn value and the amount of monomer feeding, the approximate total repeat unit number of WPA in Fig. 1a was calculated to be ~83. Meanwhile, the

number average molecular weight Mn of modified WPA with IPDI-HEA was measured to be ~12.648 kg/mol, and the polydispersity index Mw/Mn was 1.899. The effect governed the trend in relatively wide polydispersity, this also accords with our speculation, which showed that the number molecular weight (Mn) was obviously elevated after grafted of IPDI-HEA.
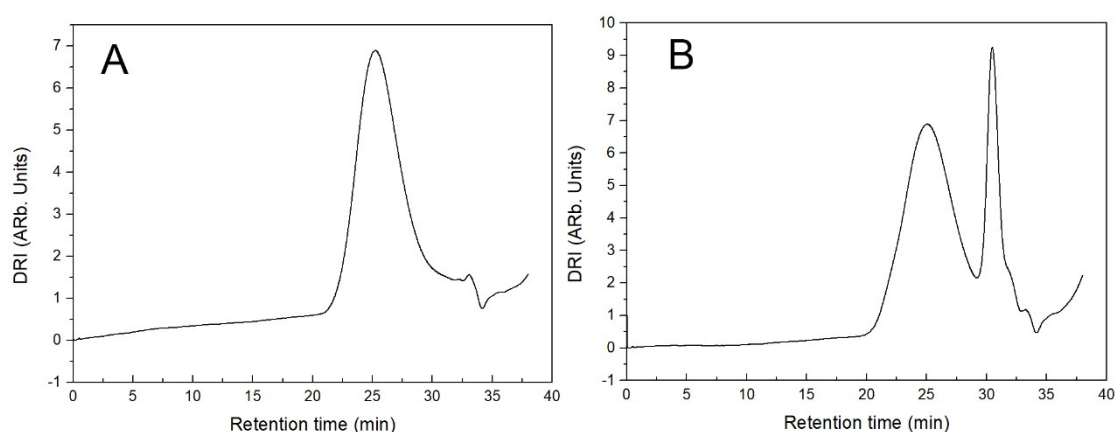
Fig. S8. SEC trace of the acrylic copolymer (A) and the unsaturated acrylic copolymer with IPDI-HEA (B).

Table S1. Molecular weight and molecular distribution of the acrylic copolymer (A) and the unsaturated acrylic copolymer with IPDI-HEA (B).

Samples	M_w	M_n	$P_d = M_w / M_n$
A	18191	10185	1.786
B	24026	12648	1.899

Table S2. The Zeta potential of modified polyacrylate dispersions

Formulations	Zeta potential (mV)
WPA	-32.1
MWPA-CDA93	-46.2
MWPA-CDA66	-53.7
MWPA-CDA39	-67.8
MWPA-PA93	-44.5
MWPA-PA66	-53.3
MWPA-PA39	-63.3

Table S3. Kinetics analysis results for photopolymerization of waterborne UV-curable EPD with CDA formulations.

Formulation	Induction time (s)	Peak maximum (s)	Conversion (%)	R (%/sec)	$\triangle$H (J/g)
WPA	1.50	5.00	33.43	1.67	159
MWPA-CDA66	1.25	4.75	39.32	1.91	217
MWPA-CDA39	1.75	5.25	36.32	1.85	204
MWPA-CDA93	1.50	5.24	39.60	1.95	242

Table S4. Kinetics analysis results for photopolymerization of waterborne UV-curable EPD with PA formulations.

Formulation	Induction time (s)	Peak maximum (s)	Conversion (%)	R (%/sec)	$\triangle$H (J/g)
WPA	1.50	5.0	33.43	1.67	159
MWPA-PA66	1.00	4.75	39.00	1.93	193
MWPA-PA39	0.75	4.25	37.50	1.83	181
MWPA-PA93	1.75	4.75	39.21	1.96	220

Table S5. Thermal stability of waterborne UV-curable EPD coatings with CDA.

Formulation	T_{max1} (°C)	T_{max2} (°C)	T_{max3} (°C)	Y_c at 600°C (%)
WPA	194.5	326	416.5	2.08
MWPA-CDA66	194.1	327.4	417.1	3.02
MWPA-CDA39	193.7	325.8	415.4	3.36
MWPA-CDA93	158.0	319.9	415.6	3.05

Table S6. Thermal stability of waterborne UV-curable EPD coatings with PA.

Formulation	T_{max1} (°C)	T_{max2} (°C)	T_{max3} (°C)	Y_c at 600°C (%)
WPA	194.5	326	416.5	2.08
MWPA-PA66	177.8	308.7	407.1	3.10
MWPA-PA39	189.2	310.2	402.1	3.24
MWPA-PA93	168.1	307.7	418.4	3.15

Table S7. The corresponding detailed data obtained from tensile measurements.

Formulations	Tensile strength (MPa)	Breaking elongation (%)	Young's modulus (MPa)
WPA	2.22	1.27	174.57
MWPA-CDA66	1.17	2.52	46.19
MWPA-CDA93	4.24	2.52	160.32
MWPA-CDA39	2.62	12.39	21.11
MWPA-PA66	3.51	2.51	147.50
MWPA-PA93	3.03	3.00	110.96
MWPA-PA39	3.81	1.91	196.75

Fig. S9. The SEM images of UV-curable waterborne EPD films with different molar content of PA. (a) MWPA-PA66, scale:200 nm; (b) MWPA-PA39, scale:30 μm; (c) MWPA-PA93, scale:200 nm.
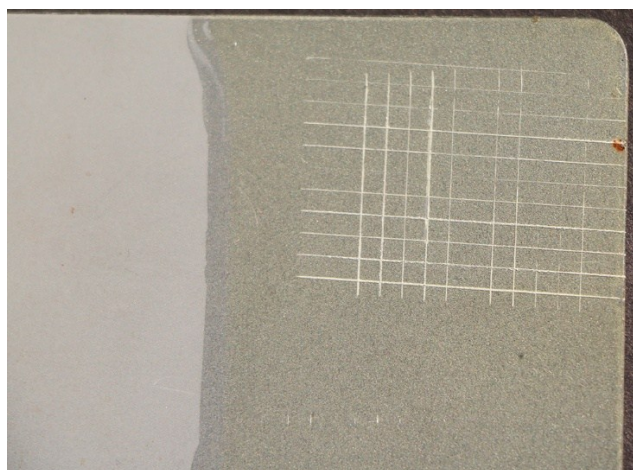

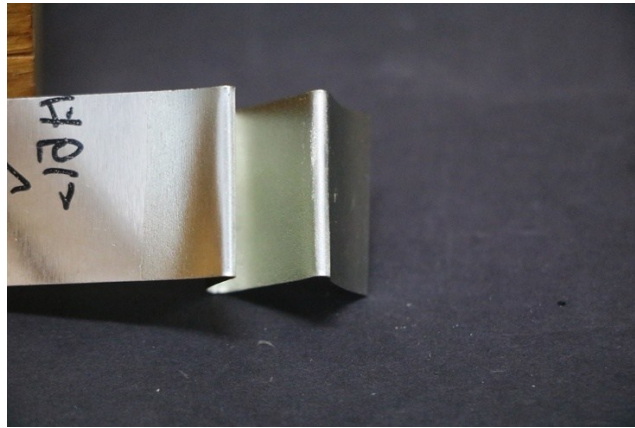**Fig. S10.** The adhesion test of UV-curable EPD coatings with pure acrylic coatings

(WPA).

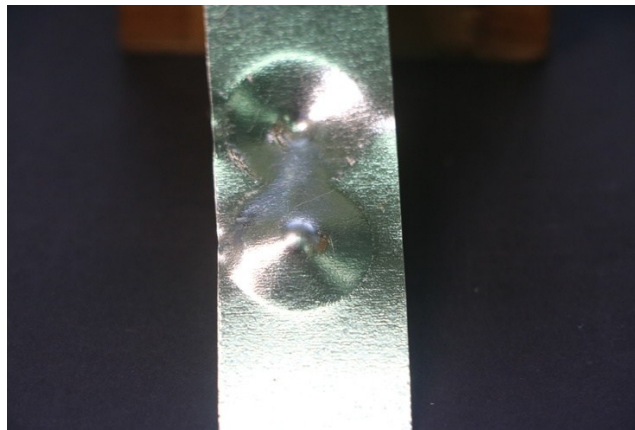**Fig. S11.** Flexibility of UV-curable EPD coating with pure acrylic coatings (WPA)

Fig. S12. The front and opposite sides of UV-curable EPD coatings with pure acrylic coatings (WPA) coated tin plate after an impact experiment.

Fig. S13. Appearance of the corroded UV-curable EPD specimen surface with pure acrylic coatings (WPA).

Table S8. General performance of the UV-curable EPD films.

Formulations	Thickness (μm)	Pencil Hardness	Glossiness/ Gs
WPA	30	2H	92.0
MWPA-CDA66	32	H	74.7
MWPA-CDA39	31	HB	46.3
MWPA-CDA93	33	2H	49.6
MWPA-PA66	32	2H	25.9
MWPA-PA39	33	3H	21.4
MWPA-PA93	31	2H	43.5