Supporting Information

Diisocyanate free and melt polycondensation preparation of bio-based unsaturated poly(ester-urethane)s and their properties as UV curable coating materials

Materials

Itaconic acid (IA) and triethanol amine were purchased from Zhejiang Guoguang Biochemistry Co. Ltd, China. 4-methoxyphenol (MEHQ), p-toluenesulfonic acid monohydrate, dibutyltin dilaurate (DBTL), 1.4-butanediamine, 1，2-ethanediamine and ethylene carbonate (EC) were obtained from Aladdin reagent, China. 1,6-hexanediamine methylene chloride acetone and chloroform were obtained from Sinopharm Chemical Reagent Co. Ltd, China. The dihydroxyurethane monomers 1,6-bis(hydroxyethyloxycarbonylamino)hexane (Urethanediol 6) and 1,4-bis(hydroxyethyloxycarbonylamino)butane (Urethanediol 4) were prepared by the reported procedure.[1] All chemicals were used as received without further purification.

Characterization

^{1}H NMR was performed on a 400MHz AVANCE III Bruker NMR spectrometer (Bruker, Switzerland).

The hydroxyl value (OHV) was defined as the number of milligrams of potassium hydroxide needed to neutralize the acetic acid formed in the acetylation of 1 g of sample and was determined according to ASTM D1957-86. The specified method involved acetylating hydroxyl groups with acetic anhydride in pyridine containing 4-dimethylaminopyridine as catalyst. After the reaction, the excess amounts of acetic

anhydride was hydrolyzed with water and titrated with an aqueous solution of potassium hydroxide (0.5mol/L). The difference between the volumes of base needed to neutralize the sample and a blank provides the hydroxyl value.

The acid value (AV) was defined as the number of milligrams of potassium hydroxide required to neutralize 1 g of sample and was determined according to ASTM D465-01 by titrating the non-volatile acid fraction of the sample with a potassium hydroxide solution in ethanol (0.1 mol/L).

The gel contents were measured using acetone extraction. The cured samples weighing between 0.42 and 0.50 g were precisely weighed (W1), extracted with acetone for 48 h under reflux using a Soxhlet extractor, and finally dried and weighed (W2). The gel content was calculated as W2/W1.

Differential scanning calorimetry (DSC) analyses were performed under nitrogen atmosphere with a calorimeter DSC1 from Mettler Toledo. The specimen was weighted in an aluminum pan and consecutively placed in the measurement heating cell. All the specimens were heated under nitrogen atmosphere from -40 to 120°C at a heating rate of 10°C min^{-1}.

Thermogravimetry (TGA) was performed on a Mettler–Toledo TGA/DSC1 Thermogravimetric Analyzer (METTLER TOLEDO, Switzerland) with high purity nitrogen or air as purge gas at a scanning rate of 10°C min^{-1} from 50°C to 600°C.

Tensile properties were evaluated by an Instron 5567 Electric Universal Testing Machine (Instron, America) with gauge length of 50mm at a cross-head speed of 5 mm min^{-1}. The specimens of 80mm×8mm×0.5mm were used for this evaluation. The

data was taken from an average of at least five specimens for accuracy.

Poly(U2-IA):

^{1}H NMR (400 MHz, D_2O, Me_4Si): 3.16 (4H, s, **NH-CH_2-CH_2-NH**), 3.33 (2H, dd, **O-CO-CH_2**), 3.68 (4H, m, **CO-O-CH_2**), 4.01-4.32 (4H, m, **NH-CO-O-CH_2**), 5.81 (H, s, **= CH_2**), 6.29 (H, s, = **CH_2**)

Poly(U4-IA):

^{1}H NMR (400 MHz, D_2O, Me_4Si): 1.44 (4H, m, **NH-CH_2-CH_2-NH**), 3.01 (4H, s, **NH-CH_2-CH_2-NH**), 3.29 (2H, m, **O-CO-CH_2**), 3.61 (4H, m, **CO-O-CH2**), 3.97-4.25 (4H, m, **NH-CO-O-CH_2**), 5.77 (H, s, = **CH_2**), 6.25 (H, s, = **CH_2**)

Poly(U6-IA):

1H NMR (400 MHz, D2O, Me_4Si): 1.24 (4H, s, **NH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH**), 1.43 (4H, t, **NH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH**), 3.03 (4H, t, **NH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH**), 3.35 (2H, s, **O-CO-CH_2**), 3.67 (4H, d, **CO-O-CH_2**), 3.98-4.30 (4H, m, **NH-CO-O-CH_2**), 5.82 (H, s, = **CH_2**), 6.30 (H, s, = **CH_2**)

Table S1 The acid value (AV) and hydroxyl value (OHV) of the prepolymers

Value	poly(U2-IA)	poly(U4-IA)	poly(U6-IA)
AV(mg KOH/g)	139	67	90
OHV(mg KOH/g)	9	17	11
M_n*(g/mol)	758	1336	1111

*$M_n = 56.1 \times 1000 \times f / (AV + OHV)$, f is the functionality of the polymer.

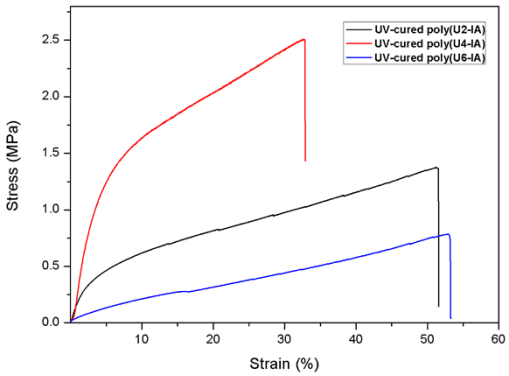

Fig. S1 Stress-strain curves of the three UV-cured polyurethane films

Table S2 Parameters of the glass transition and thermal stability of the three UV-cured polyurethane films under nitrogen atmosphere

Samples	T_g(℃)	Stage Ⅱ		Stage Ⅱ	
		Onset (℃)	T_{dmax} (℃)	Onset (℃)	T_{dmax} (℃)
UV-cured poly（U2-IA)	28	255	285	401	481
UV-cured poly（U4-IA)	21	262	288	390	483
UV-cured poly（U6-IA)	8	273	298	395	490

Table S3 TGA analysis of the three UV-cured polyurethane films under air atmosphere

Samples	Stage Ⅱ		Stage Ⅲ		Stage Ⅳ	
	Onset (℃)	T_{dmax} (℃)	Onset (℃)	T_{dmax} (℃)	Onset (℃)	T_{dmax} (℃)
UV-cured poly（U2-IA)	264	282	414	430	523	566
UV-cured poly（U4-IA)	260	288	408	435	512	555
UV-cured poly（U6-IA)	268	300	418	446	506	550

1. G. Rokicki and A. Piotrowska, *Polymer*, 2002, 43, 2927-2935.