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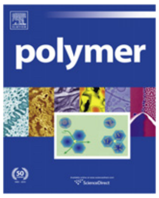

Synthesis and properties of cationic photopolymerizable hyperbranched polyesters with terminal oxetane groups by the couple-monomer polymerization of carboxylic anhydride with hydroxyl oxetane

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ABSTRACT

The hyperbranched polyesters with terminal oxetane groups were synthesized via couple-monomer methodology based on carboxylic anhydride and hydroxyl oxetane. Two competitive reactions, ring-opening reaction of carboxylic group with oxetane group and esterification of carboxylic group with hydroxyl group, occurred synchronously during the polymerization. The results showed that the hyperbranched polyesters, poly(SA-EHO) and poly(SA-EHPO), were synthesized successfully when succinic anhydride (SA) was selected to react with 3-Ethyl-3-(hydroxymethyl)oxetane (EHO) and 3-ethyl-3-((4-hydroxymethyl)phenoxymethyl)oxetane (EHPO), respectively. The degree of branching was determined to be about 0.7 for poly(SA-EHO) from the ^{1}H NMR result, which was higher than those reported in literature, indicating that the esterification was dominant. The glass transition temperatures (T_g)s were measured as −11.5 °C for poly(SA-EHO) and 14.3 °C for poly(SA-EHPO) by DSC. The number average molecular weights were 1914 g/mol and 2108 g/mol with the polydispersity indices of 2.39 and 2.28 for poly(SA-EHO) and poly(SA-EHPO), respectively. Both poly(SA-EHO) and poly(SA-EHPO) were added to bisphenol A epoxy resin, EP828, with different contents and cured under UV exposure. From the DMTA and tensile results, the UV cured poly(SA-EHPO) showed higher T_g and tensile strength compared with poly(SA-EHO) because of the existence of phenyl group in poly(SA-EHPO) chain. Moreover, both the T_gs and mechanical strength decreased, whereas the elongation percents at break increased with poly(SA-EHO) and poly(SA-EHPO) increased. This indicates that the flexibility of cured films was improved by the addition of poly(SA-EHO) and poly(SA-EHPO) in the formulations.

1. Introduction

Recently, a new approach called “couple-monomer methodology” was developed for preparing hyperbranched polymers based on the non-equal reactivity of functional groups in special monomer pairs [1–4]. This methodology does not only resolve the source of monomers but also avoid gelation usually occurring in the “A_2+B_3” approach. There have been many hyperbranched polymers synthesized through the couple-monomer methodology. Yan and Gao reported the preparation of hyperbranched poly(sulfone amine)s, poly(ester amine)s, poly(urea urethane)s, and poly(amide amine)s, and so on [5]. van Benthem group synthesized the bis(2-hydroxypropyl) amide-based hyperbranched polyesteramides via “AA’+CB_2” approach [4]. Li and co-workers reported a series of hyperbranched poly(ester-amide)s prepared from commercially available aliphatic carboxylic anhydrides or dicarboxylic acids and multihydroxyl primary amines [6,7]. Wang and co-workers synthesized hyperbranched polysiloxysilanes from A_2 and CB_2 type monomers [8,9].

UV-induced photocuring, mainly classified as cationic and radical photocuring according to the curing mechanism, has obtained important applications in many fields. The cationic photocuring possesses some advantages in contrast to the radical one, such as low shrinkage, absence of oxygen inhibition, better adhesion [10,11]. Oxetane monomers were introduced in UV curing by Crivello and Sasaki [12]. They found out that the oxetanes are generally more reactive than their structurally similar epoxy counterparts and the formulation with oxetane and epoxide possesses higher reactivity toward photoinitiated cationic polymerization [13,14]. Similar results were also reported in some other

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literatures and oxetane group is characterized to be more reactive because of not only the ring strain similar to that of epoxide but also the higher nucleohilicity than epoxy group [15–17]. Many hyperbranched polymers with cationic curable functional groups have been prepared and investigated as additives to improve the properties of the cured materials [18–21]. However, most of these hyperbranched additives were synthesized based on modification of hyperbranched polymers. Only a few cationic curable hyperbranched polymers were synthesized through polymerization of the monomers with cationic curable functional groups.

In this paper, we present the synthesis of hyperbranched polyester with terminal oxetane groups via couple-monomer methodology based on carboxylic anhydride and hydroxyl oxetane. The ring-opening reaction and esterification occur synchronously during the polymerization. The results showed that the linear or little branched polymers were obtained when cyclohexene-1,2-dicarboxylic anhydride and phthalic anhydride were selected. However, as succinic anhydride was chosen to react with hydroxyl oxetanes, the hyperbranched polyesters were synthesized successfully. The obtained hyperbranched polyesters, as additives, were added to cationic systems and cured under UV exposure. Both dynamic mechanical thermal properties and mechanical behaviors of the cured films were investigated.

2. Experimental section

2.1. Materials

3-Ethyl-3-(hydroxymethyl)oxetane (EHO) was supplied by Perstorp AB, Sweden. Cyclohexene-1,2-dicarboxylic anhydride (CHA) was supplied by Sigma–Aldrich. 3-Ethyl-3-(bromomethyl)oxetane was synthesized according to the procedure reported in the literature [22]. Bisphenol A epoxy resin, EP828, used as a cationic curable resin, was supplied by Shell Chemical Co. Irgacure 250, used as a cationic photoinitiator, was supplied by Ciba–Geigy. 4-Hydroxybenzenemethanol was supplied by Tianma Chemical Co., Suzhou, China. Acetic anhydride, 4-dimethylamino-pyridine (DMAP), succinic anhydride (SA), phthalic anhydride (PA), trimethylolpropane (TMP) and other chemicals were purchased from Shanghai First Reagent Co. All the chemicals were used as received without further purification except for EHO, which was dried with 4-Å molecular sieves before use.

2.2. Measurements

The ^{1}H NMR spectra were recorded with a Bruker 300-MHz or 400-MHz NMR spectrometer according to the research demand. $CDCl_3$ and tetramethylsilane were used as a solvent and internal reference, respectively. The average molecular weight and its polydispersity index were determined with a gel permeation chromatography (GPC) equipped with a refractive-index detector and calibrated with the standard linear PSt. DMF was used as an eluent with a rate of 1.0 mL/min. The differential scanning calorimetry (DSC) curves were recorded with a Shimazhu DSC-60 apparatus. All the samples were heated from −100 to 50 °C with a rate of 10 °C/min under nitrogen for the first scan, then cooled to −100 °C at 40 °C/min, and immediately heated at 10 °C/min from −100 °C to 50 °C again. The tensile storage modulus (E') and tensile loss factor (tan δ) were measured using a dynamic mechanical thermal analyzer (Diamond DMA, PE Co., USA) at a frequency of 2 Hz and a heating rate of 5 °C/min in the range of 0–220 °C on the sheet of $25 \times 5 \times 1$ mm^3. The crosslinking density (V_e) as the molar number of elastically effective network chain per cube centimeter of the film was calculated from the storage modulus in the rubbery plateau region according to: $\nu_e = \frac{E'}{3RT}$, where E' is the elastic storage modulus, R is the ideal gas constant, and T is the temperature in Kelvin. The mechanical properties were measured with an Instron Universal tester (model 1185, Japan) at 25 °C with a crosshead speed of 25 mm/min. The dumb-bell shaped specimens were prepared according to ASTM D412-87. Five samples were analyzed to determine an average value in order to obtain the reproducible result.

2.3. Synthesis of 3-ethyl-3-((4-hydroxymethyl)phenoxymethyl) oxetane (EHPO)

A mixture of 3-ethyl-3-(bromomethyl)oxetane (33 g, 0.184 mol), 4-hydroxybenzenemethanol (23 g, 0.184 mol), potassium carbonate (127 g, 0.920 mol) and 220 mL of DMF was poured into a glass flask equipped with a mechanical stirrer and reacted at 25 °C for 1 h and then at 70 °C for 5 h. The reaction mixture was concentrated, filtered, poured into water and then extracted for several times with dichloromethane. The combined organic layer was washed again with water, dried with anhydrous sodium sulfate, and filtrated. Finally the solvents were removed under reduced pressure. 3-ethyl-3-((4-hydroxymethyl)phenoxymethyl)oxetane (EHPO) was obtained as a pale yellow liquid with a yield of 79%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.30 (*ArH*), 6.92 (*ArH*), 4.62 (HO—CH_2—Ar—), 4.57–4.46 (*Oxetane—H*), 4.08 (—Ar—O—CH_2—Oxetane), 1.92–1.84 (CH_3—CH_2—Oxetane), 0.93 (CH_3—CH_2—Oxetane).

2.4. General polymerization procedure

A calculated amount of EHO, an equimolar amount of dicarboxylic anhydride and 2 mol% of DMAP were charged into a dry glass flask equipped with a mechanical stirrer, gas-outlet and -inlet tubes, and stirred continuously at 100 °C under N_2 atmosphere until the ^{1}H NMR signal peak at 3.79 ppm for HOCH_2-oxetane disappeared. Then the reaction temperature was raised to 150 °C. A vacuum system (about 2000 Pa) was applied to exclude the water formed during the esterification for driving the polymerization toward high conversion. The reaction was performed until the mechanical stirring became difficult. The reactant was then cooled down, and dissolved in acetone, and precipitated into deionized water twice. The precipitate was dissolved in CH_2Cl_2 again, dried with anhydrous sodium sulfate, filtrated and condensed by distillation, and finally dried at 50 °C in vacuum for 48 h to give a yellowish resin or solid.

Poly(PA-EHO) ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.82–7.31 (*Ar—H*), 4.58–4.45 (*Oxetane-H*), 4.45–4.09 (Ar—COOCH_2—), 3.62–3.20 (—CH_2—*OH*), 1.81–1.29 (CH_3—CH_2—), 1.01–0.62 (CH_3—CH_2—).

Poly(CHA-EHO) ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.58–4.45 (*Oxetane-H*), 4.31–3.85 (—CH_2—OOC—), 3.65–3.04 (—CH_2—*OH*,), 2.98–2.45 (—OOC—*CH*(hexamethylene)), 2.20–1.89 (-CH_2(hexamethylene)-), 1.89–1.14 (—CH_2(hexamethylene)—, CH_3—CH_2—), 1.01–0.75 (CH_3—CH_2—).

Poly(SA-EHO) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.51–4.38 (*Oxetane—H*), 4.26–4.20 (—COOCH_2—Oxetane-), 4.10–3.96 (—COOCH_2—), 3.59–3.42 (—CH_2—OH), 2.74–2.52 (—OOC—CH_2—CH_2—COO—), 1.78–1.70 (CH_3—CH_2—Oxetane—), 1.54–1.26 (CH_3—CH_2—), 0.95–0.74 (CH_3—CH_2—).

Poly(SA-EHPO) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.43–7.20 (*Ar—H*), 7.07–6.78 (*Ar—H*), 5.12–4.96 (—OOC—CH_2—Ar—), 4.63–4.44 (*Oxetane—H*), 4.23–4.09 (—COOCH_2—), 4.09–4.04 (—Ar—O—CH_2—Oxetane—), 3.88–3.77(—Ar—O—CH_2—C(C_2H_5)(CH_2)(CH_2)—), 3.62–3.35 (—CH_2—*OH*), 2.73–2.49 (—OOC—CH_2—CH_2—COO—), 2.49–2.12 (—CH_2—*OH*), 1.91–1.79 (CH_3—CH_2—Oxetane-), 1.63–1.40 (CH_3—CH_2—), 0.96–0.73 (CH_3—CH_2—).

2.5. End-capping of poly(SA-EHO)

4 g Poly(SA-EHO) was firstly dissolved in 40 mL of chloroform in a glass flask. 2.5 g Acetic anhydride was added, and stirred for 12 h at room temperature. Then chloroform and most of superfluous acetic anhydride were removed by distillation. The crude product was dissolved in chloroform again and washed with saturated $NaHCO_3$ aqueous solution thrice and subsequently with deionized water twice. The organic layer was collected and dried with anhydrous sodium sulfate, filtrated and condensed by distillation, and finally dried at 50 °C in vacuum for 48 h to give a yellowish resin. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.51–4.38 (*Oxetane–H*), 4.26–4.20 ($-COOCH_2-$Oxetane$-$), 4.10–3.96 ($-COOCH_2-$), 2.74–2.52 ($-OOC-CH_2-CH_2-COO-$), 2.08–2.02 ($-OOCCH_3$), 1.78–1.70 (CH_3-CH_2-Oxetane$-$), 1.54–1.40 (CH_3-CH_2-), 0.95–0.74 (CH_3-CH_2-).

2.6. Copolymerization with TMP

2.5 g SA (0.025 mol), 2.9 g EHO (0.025 mol) and 0.061 g DMAP (0.0005 mol) were charged into a dry glass flask equipped with a mechanical stirrer and gas-outlet and -inlet tubes, and stirred continuously at 100 °C under N_2 atmosphere until the ^1H NMR signal peak at 3.79 ppm for $HOCH_2-$oxetane disappeared. The product was collected as a monomer for copolymerization.

0.1865 g TMP (0.00139 mol) was charged into a dry glass flask equipped with a mechanical stirrer and an isobarical dropping funnel, and placed into a pre-heated (150 °C) oil bath. Then a vacuum was applied. The monomer obtained above was dropped with a rate of about 2 g/h through the isobarical dropping funnel and reacted for another 3.5 h. Then the cooled mixture was dissolved in acetone and precipitated into deionized water twice. The precipitate was dissolved in CH_2Cl_2, dried with anhydrous sodium sulfate, filtrated and condensed by distillation, and finally dried at 50 °C in vacuum for 48 h to give a yellowish resin.

Copoly(SA-EHO) ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.51–4.38 (*Oxetane–H*), 4.26–4.20 ($-COOCH_2-$Oxetane$-$), 4.10–3.96 ($-COOCH_2-$), 3.59–3.42 ($-CH_2-OH$), 2.74–2.52 ($-OOC-CH_2-CH_2-COO-$), 1.78–1.70 (CH_3-CH_2-Oxetane$-$), 1.54–1.26 (CH_3-CH_2-), 0.95–0.74 (CH_3-CH_2-).

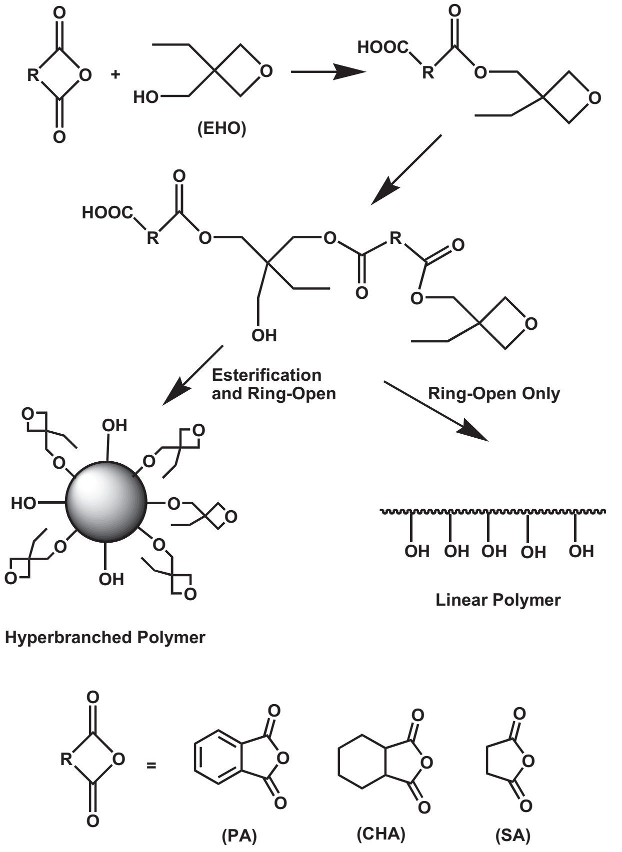
3. Results and discussion

3.1. Polymerization of carboxylic anhydride and hydroxyl oxetane

Nishikubo and co-workers have done systematic and extensive investigation on the reactions of oxetanes with protonic and aprotic compounds, including carboxylic acid, phenol, thiol, acyl chloride, thioester, phosphonyl dichloride, silyl chloride and chloroformate [23–27]. Several molecular structure-controlled polymers have been prepared through these reactions. The linear and hyperbranched polyesters with pendant primary hydroxyl groups were prepared by the reaction of bis(oxetane) with dicarboxylic acid and 1,3,5-benzenetricarboxylic acid via an $A_2 + B_3$ approach, respectively. The ester bond in the polymer chain was formed via ring-opening polyaddition of carboxylic acid and oxetane group, generating pendant primary hydroxyl group, simultaneously. The formed hydroxyl group failed to react further with carboxylic group under the condition.

However, in our opinion, the esterification might easily occur as removing water from the vessel, or adding a catalyst. Thus, every reacted hydroxyl group can be considered as a branched point, resulting in the formation of highly branched polymers.

As shown in Scheme 1, as the equimolar amount of dicarboxylic anhydride reacted with EHO at lower temperature, an intermediate compound with one carboxylic group and one oxetane group was produced, considered as a latent ABB' type monomer. After raising the reaction temperature and applying vacuum to the vessel, the ring-opening reaction occurred further, leading to the formation of a dimer with one carboxylic acid group, one hydroxyl group and one oxetane group. Then both oxetane groups and hydroxyl groups may react with carboxylic acid groups. Two kinds of reactions, ring-opening reaction of carboxylic group with oxetane group and esterification of carboxylic group with hydroxyl group, occur during the polymerization. If only the former ring-opening reaction happened, a linear polymer with pendant primary hydroxyl groups can be prepared, which is similar to the result reported by Nishikubo. However, if the esterification occurs synchronically, a branched polymer with both oxetane and hydroxyl groups can be obtained. When the rate of esterification is much higher than that of ring-opening reaction, most of the hydroxyl groups formed during ring-opening reaction can be reacted with carboxylic acid groups rapidly, resulting in the formation of hyperbranched polymer with high degree of branching (DB). This may overcome the disadvantage of low DB of hyperbranched polymers prepared via one-pot method of AB_x type monomers.



Scheme 1. Schematic illustration for ideal polymerization route of carboxylic anhydride and hydroxyl oxetane.

Alicyclic, aromatic, and aliphatic dicarboxylic anhydrides were selected to prepare a series of polymers, as shown in Scheme 1. Fig. 1 shows the ^1H NMR spectra of poly(PA-EHO) and poly(CHA-EHO). As mentioned above, some residual oxetane rings still exist in the system whereas most of the hydroxyl groups were consumed when a hyperbranched polymer was obtained. However, the signal peaks attributed to proton on the oxetane rings of both poly(PA-EHO) and poly(CHA-EHO) at 4.58–4.45 ppm are very weak. Moreover, the signals corresponding to the methylene proton next to hydroxyl group are obvious. From the spectrum of poly(CHA-EHO), the integrations of the proton attributed to oxetane ring,

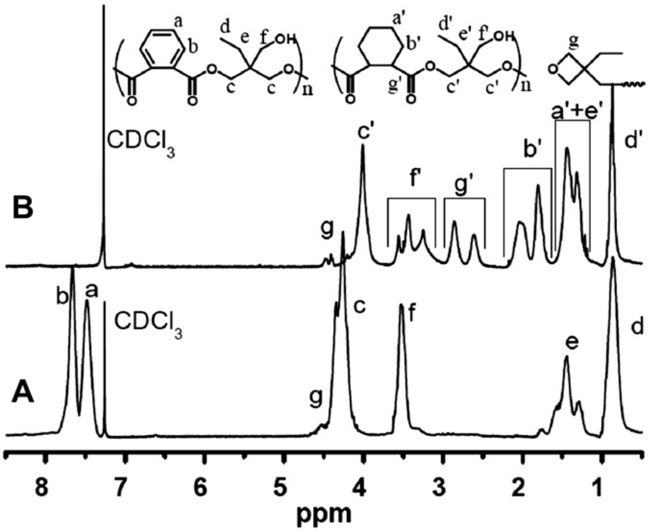


Fig. 1. ^{1}H NMR spectra of (A) poly(PA-EHO) and (B) poly(CHA-EHO).

methylene adjacent to ether bond, methylene adjacent to hydroxyl group, and methyl are 2.64, 37.94, 19.42, and 30.00, respectively. This indicates that more than 93% oxetane groups are consumed in the polymerization but most of the hydroxyl groups did not react with carboxylic acid groups. All the facts suggest that a linear or little branched polymer was obtained when PA or CHA was chosen.

In contrast, when SA, an aliphatic dicarboxylic anhydride, was selected, the distinct results were obtained. As shown in Fig. 2, the signal peaks attributed to the oxetane proton at 4.58–4.45 ppm are obvious and the signals at 3.59–3.42 ppm originated from the methylene unit adjacent to hydroxyl group are much weaker than those for poly(PA-EHO) and poly(CHA-EHO). The integrations of the proton attributed to oxetane ring, methylene adjacent to ether bond, methylene adjacent to hydroxyl group, and methyl were obtained to be 12.90, 40.42, 7.13, and 30.00, respectively. This indicates that about one third oxetane groups exist in the final product and more than half of the hydroxyl groups formed during the reaction were consumed by the reaction with carboxylic acid groups. A hyperbranched polymer was finally prepared by polymerization of SA and EHO.

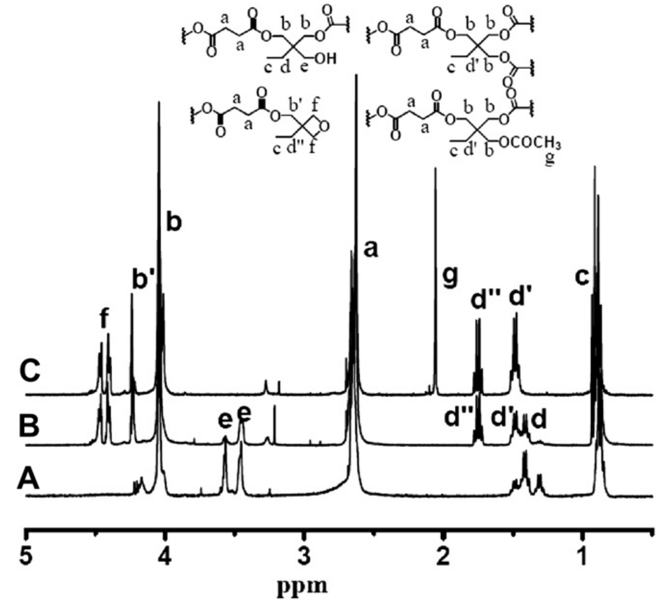


Fig. 2. ^{1}H NMR spectra of (A) poly(SA-TMP), (B) poly(SA-EHO) and (C) end-capped poly (SA-EHO).

3.2. DB, M_n of hyperbranched poly(SA-EHO)

DB is an important parameter for the structural characterization of a hyperbranched polymer. Theoretically, the DB of a hyperbranched polymer is 0.5 when one-pot polymerization of an AB_2 monomer is employed [28]. However, this value is obtained based on the assumption of equal reactivity of two B functional groups. In fact, the reactivity of the residual B functional group becomes lower after the other one has reacted because of steric effect or some other reasons. Consequently, the hyperbranched polymers prepared in experiments have lower DB than the theoretical value, usually in the range from 0.3 to 0.5. Several methods have been reported to improve DB, such as higher reactivity of linear vs. terminal units, polymerization of prefabricated dendron monomers, slow addition techniques, and polymerization in the presence of core molecules [29,30]. However, most investigations on these methods were based on theoretical calculation and only a few hyperbranched polymers with high DB (more than 0.5) were reported. A. Hult reported the synthesis of hyperbranched aliphatic polyesters with the DB value of about 0.8 based on 2,2-bis(methylol)propionic acid and tris(methylol)propane as a core molecule [31]. Mario Smet and Mitsuru Ueda synthesized hyperbranched poly(arylene oxindole)s and hyperbranched polythiolketal both with 100% DB, respectively [32–34].

Fortunately, DB of poly(SA-EHO) can be calculated through ^{1}H NMR spectrum directly when a Bruker 400-MHz NMR spectrometer was used (Fig. 2). It is clear that three groups of the peaks at around 1.76, 1.49 and 1.42 ppm are attributed to the methylene proton adjacent the methyl group of three different units. As well-known, the peak for the terminal unit has the highest chemical shift because of the oxetane ring next to the methylene group. The peak for the dendritic unit has a high chemical shift compared with that of the linear one because of the higher electronegativity of ester bond group than hydroxyl group. To confirm the above presumption, end-capping of the hydroxyl groups with acetic anhydride was conducted. The ^{1}H NMR spectrum of end-capped product is also given as the curve C in Fig. 2. The peak signals at 1.42 and 3.35–3.62 ppm disappeared and a new single peak signal at 2.06 ppm corresponding to the methyl proton attached to the ester carbonyl appears, suggesting that the above presumption is exactly true. Surprisingly, the integration of signal attributed to the dendritic unit was much larger than that corresponding to the linear unit, which is quite different from usual hyperbranched polymers reported in literature. The DB value was calculated from $DB = (T + D)/(T + L + D)$ to be 0.67, and that calculated from $DB = 2D/(2D + L)$ was 0.70. These values are higher than both the usual value of 0.30–0.50 and the theoretical value of 0.5 via one-pot polymerization of an AB_2 monomer. This indicates that the rate of esterification reaction was higher than that of ring-opening reaction. As a contrastive experiment, equimolar TMP, instead of EHO, was polymerized with SA under the same condition. The ^{1}H NMR spectrum of poly(SA-TMP) is also shown as the curve A in Fig. 2. In contrast, the integration of signal attributed to the dendritic unit is much less than that corresponding to the linear unit and the DB value calculated according to Frey was only 0.42.

The glass transition temperature (T_g) of the obtained hyperbranched poly(SA-EHO) was determined by DSC to be around −11.5 °C. The average molecular weight (M_n) and its polydispersibility index (PDI) were measured with GPC spectroscopy although this method is limited because of the calibration with standard linear PSt. The results are listed in Table 1. The M_n of

Table 1
Product yields and characters of hyperbranched polyesters.

Polymer	Yield (%)	DB	M_n (g/mol)	PDI	T_g (°C)
Poly(PA-EHO)	82	–	–	–	–
Poly(CHA-EHO)	86	–	–	–	–
Poly(SA-EHO)	82	0.70	1914	2.39	−11.5
CoPoly(SA-EHO)	79	0.67	2300	1.60	−9.9
Poly(SA-EHPO)	81	–	2108	2.28	14.3

hyperbranched poly(SA-EHO) is 1914, perhaps being underestimated, and the polydispersity index is 2.39. To obtain a hyperbranched polymer with higher molecular weight, higher reaction temperature and longer reaction time were considered. However, higher molecular weight product could not be obtained and gelation occurred under both conditions. The lower molecular weight of the polymer is probably due to some intramolecular reactions and the gelation was probably caused by some side reactions such as intermolecular etherification between two hydroxyl groups or a hydroxyl group and an oxetane group.

3.3. Copolymerization of SA-EHO with TMP

To avoid gelation and obtain a hyperbranched polymer with higher molecular weight, the copolymerization approach was considered. A. Hult developed the copolymerization of 2,2-Bis (hydroxymethyl)propionic acid (bis-MPA) with a polyol core, and found that the risk of gelation was greatly reduced [31,35,36]. However, the gelation occurred when SA-EHO as a monomer was copolymerized with TMP as a three-functional core molecule. The reaction parameters and characters of a typical soluble copolymer, which were measured before gelation, are listed in Table 1. The average molecular weight of the copolymer is 2300, bigger than that of poly(SA-EHO), but having a narrow polydispersity of 1.6.

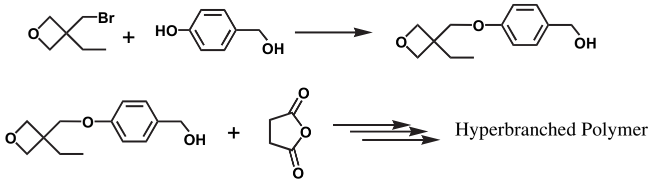
3.4. Cationic curing

The hyperbranched poly(SA-EHO) was investigated as an additive in cationic UV-curing systems. The samples containing different ratios of poly(SA-EHO) to EP828 and 2 wt.% cationic photoinitiator were prepared (Table 2), and exposed to a medium pressure mercury lamp to obtain the cured films. However, as the content of poly(SA-EHO) increased, the curing of the formulation became difficult. When the ratio reached to 30%, the film couldn't cure completely even with a long UV exposure time. This is interpreted to be due to the influence of the carbonyl group on the ester bond adjacent to the oxetane ring [37,38]. The carbon atom on the oxetane ring became more electron-deficient after the oxetane ring was activated by protonic acid while the oxygen atom on the carbonyl group was electron-rich. The oxygen atom attacked the carbon atom, resulting in the formation of a stable six-member ring. This side reaction played an important role and gave rise to deactivation of oxetane groups.

To avoid the side reaction, a new hydroxyl oxetane, EHPO, was synthesized to prepare a novel polymer, poly(SA-EHPO) (Scheme 2).

Table 2
Viscoelastic properties of the cured EP828/Poly(SA-EHO) films.

Sample	Formulation (wt.%)		FWHM (°C)	V_e (mmol/cm^3)
	EP828	Poly(SA-EHO)		
$EP_{100}PSE_0$	100	0		
$EP_{95}PSE_5$	95	5	21.5	5.37
$EP_{90}PSE_{10}$	90	10	24.7	4.79
$EP_{85}PSE_{15}$	85	15	23.4	4.56
$EP_{80}PSE_{20}$	80	20	25.8	3.92



Scheme 2. Synthesis routes of EHPO and Poly(SA-EHPO).

The ^{1}H NMR spectra of EHPO and poly(SA- EHPO) were shown as Figs. 3 and 4, respectively. The DB couldn't be calculated directly according to the ^{1}H NMR result, which may be due to the influence of benzene ring in the polymer chain. However, the peak attributed to proton on oxetane ring exits and the signal corresponding to the methylene adjacent to hydroxyl group is weak. This indicates that the hyperbranched polymer, poly(SA-EHPO) was obtained. The average molecular weight and its polydispersity were also characterized with GPC and to be 2108 g/mol and 2.28, respectively. The T_g of poly(SA-EHPO) was determined to be higher than those of poly (SA-EHO) and copoly(SA-EHO). The reason is presumed to be the benzene ring in the main chain of poly(SA-EHPO).

In poly(SA-EHPO), the ester bond which makes the cationic curing activity of oxetane groups decreased is replaced by ether bond and the deactivation effect will not occur, which enhance the cationic UV-curing.

3.5. Properties of the UV cured films

The formulations containing different ratios of EP828 to poly (SA-EHO) or poly(SA-EHPO) were prepared with the addition of 2 wt.% cationic photoinitiator Irgacure 250, and exposed to a medium pressure mercury lamp (2 KW, Fusion UV systems, USA) to obtain the cured films. For EP828/poly(SA-EHO) system (Table 2), a series of EP_mPSE_n were obtained, where m is the percent content of EP828, and n is the percent content of poly(SA-EHO). For EP828/poly(SA-EHPO) system, another series of EP_pPSEP_q were obtained, where p is the percent content of EP828, and q is the percent content of poly(SA-EHPO).

The dynamic mechanical thermal analysis was employed to investigate the dynamic mechanical behavior of the cured films.

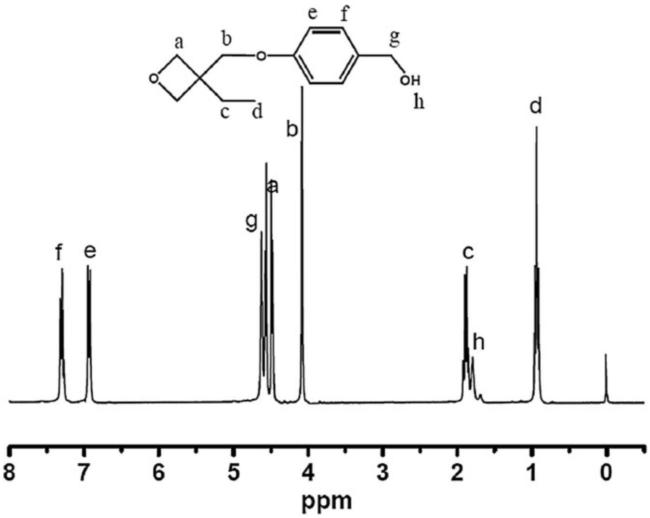


Fig. 3. ^{1}H NMR spectrum of EHPO.

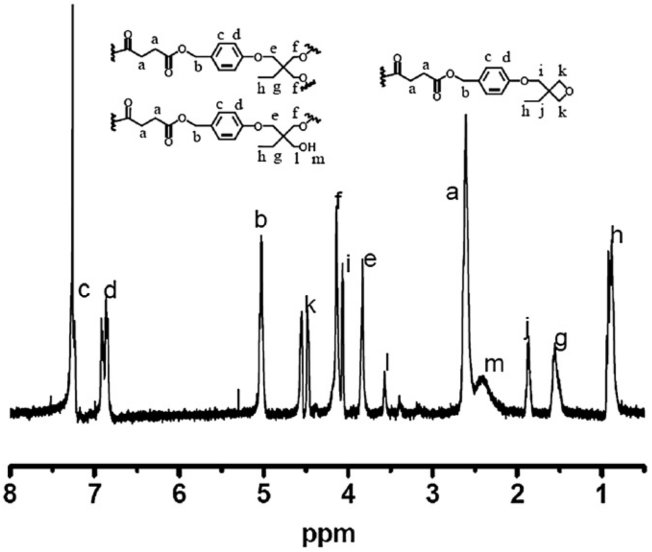


Fig. 4. ^{1}H NMR spectrum of poly(SA-EHPO).

The storage modulus and loss factor (tan δ) curves of cured EP828/poly(SA-EHO) films are shown in Fig. 5 and the detailed results are listed in Table 2. The crosslinking density (V_e) is the molar number of elastically effective network chains per cubic centimeter of the cured film. The T_g can be defined as the temperature at which the peak of tan δ curve appears. As listed in Table 2, the crosslinking density of cured film decreases with the content of hyperbranched poly(SA-EHO) increasing. This behavior can be attributed to two reasons. On the one hand, the relative concentration of oxetane group in poly(SA-EHO) is lower than that of epoxy group in EP828 resin. On the other hand, the oxetane group of poly(SA-EHO) has lower cationic UV-curing activity because of the deactivation effect of the carbonyl group on the ester bond adjacent to the oxetane ring. The T_g of cured film decreases continuously from 140 °C for pure EP828 to 104 °C for 20 wt.% poly(SA-EHO) addition. This can also be ascribed to two factors. Firstly, the crosslinking density decreases with the content of hyperbranched poly(SA-EHO) increasing. Secondly, the hyperbranched poly(SA-EHO) chain is aliphatic while EP828 is an aromatic resin. As a result, the incorporated hyperbranched poly(SA-EHO) can reduce the rigidity of the formed network and make chain motion possible at lower temperature.

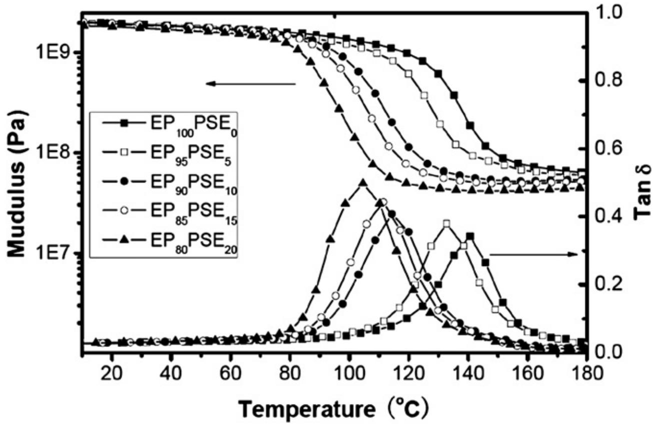


Fig. 5. DMTA curves of cured EP828/Poly(SA-EHO) films with different Poly(SA-EHO) contents.

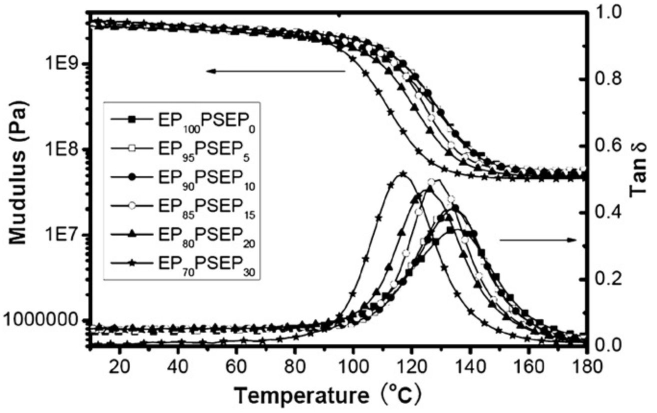


Fig. 6. DMTA curves of cured EP828/Poly(SA-EHPO) films with different Poly(SA-EHPO) contents.

Moreover, it is well known that the value of tan δ is the ratio of viscous modulus to elastic modulus and that the peak value of tan δ curve can be used to predict the damping behavior of a material. As shown in Fig. 5, the peak value of tan δ increases with an increasing weight fraction of poly(SA-EHO). This indicates that the cured film with higher content of poly(SA-EHO) has higher damping property. The breadth of the glass transition can be defined by the full width at half maximum (FWHM) of the tan δ peaks. As listed in Table 2, all the FWHMs of the peaks are in a temperature range of 23.5 ± 2.5 °C. The uniformity of the tan δ peak indicates the absence of any network heterogeneity, which implies the good miscibility between poly(SA-EHO) and EP828.

The EP828/poly(SA-EHPO) cured films are also tested via dynamic mechanical thermal analysis and the results are given in Fig. 6 and Table 3. It is interesting to note that the crosslinking density of the cured films first increases and then decreases with the increasing of poly(SA-EHPO). The increase in the crosslinking density along with poly(SA-EHPO) addition may be due to the higher reactivity of the oxetane group in poly(SA-EHPO), compared with epoxy group in EP828 [13–17]. Due to the small amount of oxetane group in the formulation and overlapping of peaks in the range of 940 cm^{-1} to 1097 cm^{-1} for oxetane and other ether bonds, as shown in Fig. 7, the investigation of relative reactivity and the polymerization kinetics were failed with the real-time FT-IR spectroscopic analysis. Moreover, it is found that the further addition of poly(SA-EHPO) makes the crosslinking density of cured film decreasing. That can be attributed to two factors. On the one hand, the relative concentration of reactive group in poly(SA-EHPO) is much lower than that in EP828 resin. On the other hand, the hydroxyl group in poly(SA-EHPO) can react with the growing chain through the chain transfer mechanism, resulting in the decrease in the formed polymeric chain length, thus the lower crosslinking density of the cured film [39]. The T_g of cured films decreases with poly(SA-EHPO) content increasing. That's mainly due to the less

Table 3
Viscoelastic properties of the cured EP828/Poly(SA-EHPO) films.

Sample	Formulation (wt.%)		FWHM (°C)	V_e (mmol/cm^3)
	EP828	Poly(SA-EHPO)		
$EP_{100}PSEP_0$	100	0	29.8	4.58
$EP_{95}PSEP_5$	95	5	26.4	5.06
$EP_{90}PSEP_{10}$	90	10	26.4	4.80
$EP_{85}PSEP_{15}$	85	15	22.6	4.75
$EP_{80}PSEP_{20}$	80	20	24.7	4.36
$EP_{70}PSEP_{30}$	70	30	23.7	4.13

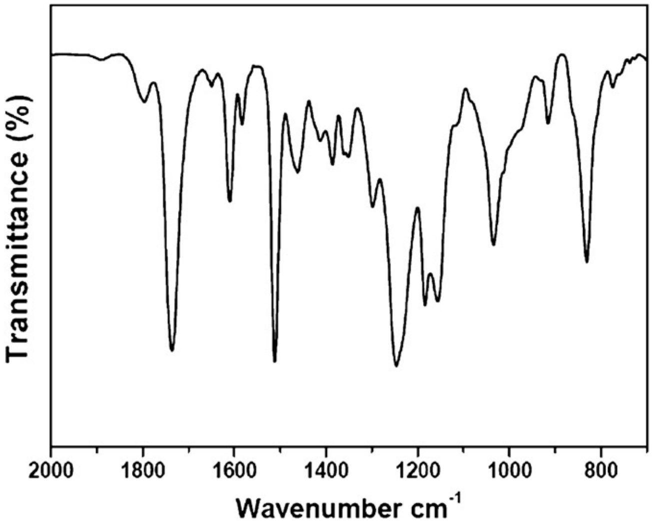


Fig. 7. FT-IR spectrum of $EP_{50}PSEP_{50}$ formulation.

rigid polymer chain in poly(SA-EHPO). The peak value of tan δ also increases with the weight fraction of hyperbranched poly(SA-EHPO) increasing, which implies that the cured film with higher content of hyperbranched poly(SA-EHO) has higher damping property. The glass transitions of the cured films keep narrow, indicating that the hyperbranched poly(SA-EHPO) and EP828 have good compatibility.

The mechanical properties of cured films were measured via tensile test and the results are listed in Table 4. The tensile strength and elongation at break are mainly influenced by the crosslinking density and the rigidity of the network chains. Both the tensile strength and elongation at break decrease when poly(SA-EHO) was added. That's because both the crosslinking density and the rigidity of the formed network decrease. However, when a small amount of poly (SA-EHPO) was added, the increasing of the crosslinking density, as discussed above, makes the tensile strength increased. As the content of poly(SA-EHPO) increases continuously, the tensile strength decreases due to the decrease of aromatic group concentration in the formulation and thus the rigidity. The elongation at break always increases for both systems, suggesting that the increased flexibility of the network is the primary factor in the change.

In particular, the cured EP828/poly(SA-EHPO) films have higher tensile strength and lower elongation at break than EP828/poly(SA-EHO) films when the same contents of polymers were added. That's attributed to two factors, the reactivity of oxetane group and the rigidity of the polymer chain.

Table 4
Tensile strength and elongation at break of the cured EP828/Poly(SA-EHO) and EP828/Poly(SA-EHPO) films.

Samples	Tensile strength (MPa)	Elongation at break (%)
EP_{100}	64.9 (1.9)	3.1 (0.2)
$EP_{95}PSE_{5}$	59.1 (3.2)	3.7 (0.6)
$EP_{90}PSE_{10}$	52.8 (2.5)	5.1 (0.2)
$EP_{85}PSE_{15}$	43.3 (3.7)	7.1 (0.7)
$EP_{80}PSE_{20}$	36.9 (2.3)	7.9 (0.4)
$EP_{95}PSEP_{5}$	69.7 (3.5)	3.4 (0.3)
$EP_{90}PSEP_{10}$	64.1 (2.7)	3.8 (0.3)
$EP_{85}PSEP_{15}$	58.1 (4.2)	4.5 (0.6)
$EP_{80}PSEP_{20}$	52.7 (3.1)	5.2 (0.5)
$EP_{70}PSEP_{30}$	42.9 (3.9)	7.2 (0.9)

Standard deviation listed in parenthesis.

4. Conclusion

Two competitive reactions, ring-opening reaction and esterification, between carboxylic anhydride and hydroxyl oxetane took place during the polymerization. In this work, it was found that a linear or little branched polymer was obtained when cyclohexene-1,2-dicarboxylic anhydride and phthalic anhydride were selected as monomers. However, when succinic anhydride was used as a monomer, the hyperbranched polyester, poly(SA-EHO), was synthesized successfully. The obtained poly(SA-EHO) has a higher DB of about 0.7 than that reported in literature, calculated directly according to the ^{1}H NMR result. This indicates that the rate of esterification was much higher than that of ring-opening reaction. The T_g of poly(SA-EHO) was $-11.5\,^{\circ}$C from DSC. And the average molecular weight was determined to be 1914 g/mol, perhaps being underestimated, with the polydispersity index of 2.39. The hyperbranched poly(SA-EHPO) with aromatic component was also prepared. Both hyperbranched polyesters were added to EP828 resin as additives with different contents, and cured by the exposure to a UV lamp, respectively.

The T_g measured by DMTA and tensile strength decrease with increasing poly(SA-EHO) in the cured EP828/poly(SA-EHO) film. However, for EP828/poly(SA-EHPO) film, the T_g decreases, but the tensile strength increases with the addition of a small amount of poly(SA-EHPO), and then decreases with further addition. The EP828/poly(SA-EHPO) films have higher tensile strength and lower elongation at break than EP828/poly(SA-EHO) films.

Acknowledgements

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