Linear Bio-Based Water Soluble Aromatic Polymers from Syringic Acid, S Type Degradation Fragment from Lignin

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ABSTRACT: Degradation products of lignin, a widely available biopolymer, represent the most abundant feedstock for aromatics in nature. In this work, we focused on syringic acid, derived from lignin S-type monolignol, to synthesize different monomers for radical polymerization. The resulting polymers have molecular weight spanning over a wide range, which depends on the monomer, with up to M_n = 1,100,000 g.mol^{-1} and $Đ$ = 3.0. The novel polymers exhibit a thermal stability higher than 350°C and differentiated glass transition temperatures, ranging from 105 to 120°C. One of the monomers synthesized with a free carboxyl group was able to polymerize in water—instead of organic solvent—and resulted in a water soluble polymer. Monomers from syringic acid offer a unique bio-based alternative to oil-based polystyrene in industry for a wider range of application. © 2020 Wiley Periodicals, Inc. J. Polym. Sci. **2020**, *58*, 540–547

KEYWORDS: biomass; lignin; phenol; polymers; renewable

INTRODUCTION Bio-based polymers are of growing interest as alternatives to petroleum plastics. Polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polystyrene (PS) constitute the top five polymers produced worldwide[1] and their renewable alternatives have been widely studied.[2–5] However, the emergence of aromatic biopolymer as polystyrene replacement has been hindered by the restricted availability of aromatic compounds in biomass. Lignin, the second most abundant biopolymer on earth, is a polyphenol highly recalcitrant to depolymerization due to its extremely heterogeneous and crosslinked structure. This natural macromolecule results from the oxidative polymerization of three monomers also known as monolignols, namely *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol; their ratio depends on the type of plant and environmental factors (Fig. 1). Once polymerized, those monolignols form three different types of monomeric units labeled H, G or S units, respectively. By extension, after lignin degradation, the small depolymerized products can also be labeled S, G or H-type fragments based on the number of methoxy goup in positions 3 and 5 of the aromatic. Recent advances in depolymerization technics and purification processes now enable the use of a large range of aromatic compounds as bio-sourced platform chemicals.

Several phenols have already been successively isolated from lignin and considered for polymerization. The main studied strategy is generally poly-condensation. The resulting polymers are typically studied as bio-renewable alternatives to polycarbonate or polyethylene terephthalate.[6–8] With this approach, inclusion of the arene structure in the polymer chain and the addition of comonomer offers great tunability of the final polymer properties. However, functionalization and copolymerization often largely increase the ultimate petroleum-based fraction in the final composition.

Another approach to aromatic polymer synthesis is to use the aromatic ring as the side chain, as in PS. Bio-based polymers with PS-like configuration offer several advantages as compared to the polycondenzation method. Simple one-step monomer functionalization combined with the elimination of comonomer allows to synthesize aromatic-rich polymers with an overall much greener process and very high loading of renewable material. Furthermore, monomer synthesis typically leaves one functional group unreacted (phenol or side chain) allowing for wider application such as post-functionalisation. Such a configuration permits free-radical polymerization or other chain growth polymerization.

S and G-type lignin degradation fragments include small phenol compounds such as vanillin and syringic acid (SA). Many

Additional supporting information may be found in the online version of this article.

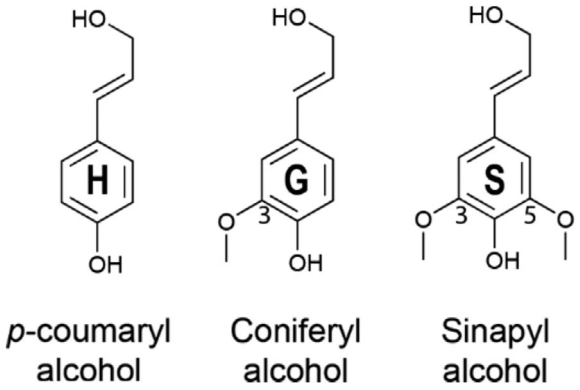

FIGURE 1 Three lignin monolignol responsible for the creation of (from left to right) *p*-coumaryl, guiacyl, and syringyl units. After depolymerisation, those units will yield H, G, or S type lignin degradation fragments, respectively.

studies have focused on vanillin as platform chemical for synthesizing bio-based aromatic polymers.[8–14] Fache et al. extensively reviewed different functionalization strategies to create different monomers for polycondenzation and radical polymerization. The 22 monomers can then be used for the synthesis of bio-based polyester, polyurethanes, non-isocyanate polyurethanes (NIPU), and epoxy polymers.[15] S-type phenols, despite being a major degradation product of lignin from hardwood, have only recently attracted attention as bio-renewable feedstock. Epps et al. studied the polymerization of monomer from syringol.[16] This work further highlighted that similar monomer synthesized from G-type compound—vanillin, guaiacol, 4-methylguaiacol and 4-ethylguaiacol—result in polymers with different properties. Copolymerization allows fine tuning of physicochemical or thermal properties, such as glass transition temperature or intrinsic viscosity to fit applications. Phenolic compounds with aldehyde or aliphatic side chains have been identified as a product of lignin pyrolysis.[17–19] However, as milder and greener depolymerization processes gain traction, phenolic depolymerization product tend to be less degraded and retain most of their functional group. Phenolic compound from oxidative degradation with acid or aldehyde group now offer more possibilities for monomer synthesis and polymer functionalization.

In this work, we present the synthesis of several novel linear polymers with PS-like structure from biomass feedstock. To the best of our knowledge, functionalization and polymerization of S type degradation fragment with carboxylic acid functional group has never been reported. Two different strategies were considered for functionalization by attaching an alkene group on either the acid group or the phenol function. Although the former strategy required further protection, polymerization yielded a pure white and high-molecular-weight polymer. Functionalization through the phenol group allowed the resulting monomer to be polymerized in aqueous medium and yielded a water soluble polymer. Thermal analysis showed high thermal stability and a glass transition temperature ranging from 105 to 120°C. Application in water soluble paint to replace the polymeric binder and possible use in water treatment will be studied in a future study.

RESULTS AND DISCUSSION

Functionalization through Acid Group

As a first step to create aromatic polymer from SA, a monomer with unsaturation has to be synthesized. Two clear pathways for functionalization are to make use of either the phenolic group on C4 or the carboxyl group on C1. Phenol reactivity is known to be low and SA furthermore showcases risk of deactivation by steric hindrance from the two adjacent methoxy groups. For these reasons, the vinyl group was added by reaction with the carboxylic acid as shown in Figure 2.

Vinylbenzyl chloride reaction in DMF with SA yielded compound **1** with 84% yield. However, a high amount of di-reacted SA was also formed. Formation of ether bond in the phenol position was confirmed by NMR and mass spectroscopy (Figures SI1 and SI2). Direacted SA compound is not desired as even a small amount will lead to crosslinking reaction during radical polymerization. Ten times excess of SA successfully and entirely removed the side reaction (purity >99%), while more than 95% of the unreacted SA could be recovered and be reused.

Screening of solvent and initiator for compound **1** could not point out suitable conditions for free-radical polymerization (Table 1). The resulting molecular weight after reaction could not be obtained higher than M_n = 2,300 g.mol^{-1}. NMR analysis indicated that more than 86% of the treated monomer still exhibited an intact vinyl group. Phenolic compound are well known for their antioxidant and radical scavenging properties[20–23] due to the resonance in the aromatic ring and the formation of quinone stabilizing the overall structure (Fig. 3). Thus it is highly probable that although the two adjacent methoxy groups were thought to hinder that effect, the phenol captures radical after the initiation step, quickly leading to termination of the polymerization.

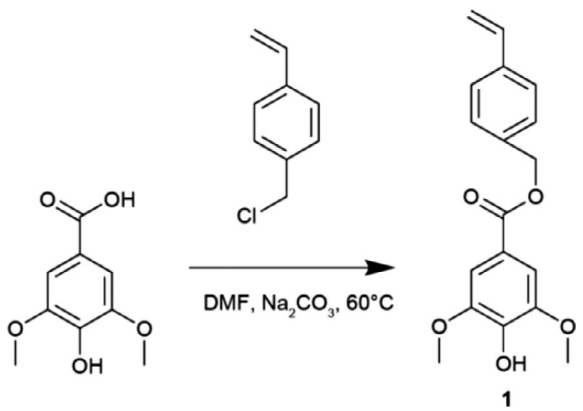

FIGURE 2 Synthesis of compound **1** by reaction of SA with vinyl benzyl chloride in DMF.

TABLE 1 Polymerization screening for compound **1**

Polymerization medium	Initiator	M_n (g.mol^{-1})
Bulk	AIBN	1,650
Bulk	ACCN	1,700
Bulk	Benzoyl peroxide	2,300
Bulk	Dicumyl peroxide	1,400
Ethylene glycol	AIBN	800
Ethylene glycol	ACCN	800
Ethylene glycol	Benzoyl peroxide	800
Ethylene glycol	Dicumyl peroxide	1,600
Xylene	AIBN	800
Xylene	ACCN	800
Xylene	Benzoyl peroxide	800

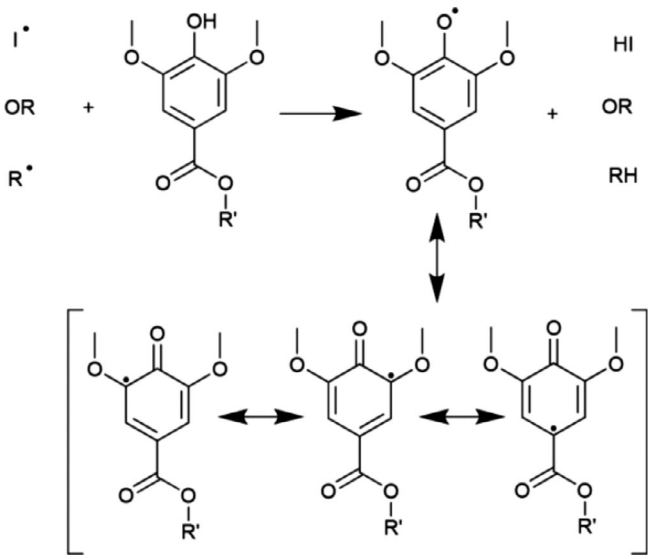

FIGURE 3 Radical scavenging behavior of compound **1**. Activated initiator species (I•) and growing chain (R•) are deactivated by the capture of radical. The resulting structure is stabilized by resonance and can no longer participate in the polymerization.

To favor the propagation reaction during the polymerization, the phenol group has to be protected. Two pathways were explored to eliminate the radical scavenging properties of compound **1** and enable free-radical polymerization. Protection by acetic anhydride and benzoyl chloride lead to compounds **2** and **3**, respectively, with high yield and high purity (Fig. 4).

After screening for different polymerization conditions compounds **2** and **3** proved to exhibit two contrasting polymerization behaviors. The acetyl protected compound **2** was polymerized up to M_n = 4,000–5,000 g.mol^{-1}, while compound **3** reached up to M_n = 1,100,000 g.mol^{-1}, (Table 2, Figs. 5 and 6). The resulting polymer formed a surprisingly pure white fluffy powder, while the high content in aromatic rings was rather expected to yield an orange/yellowish compound.

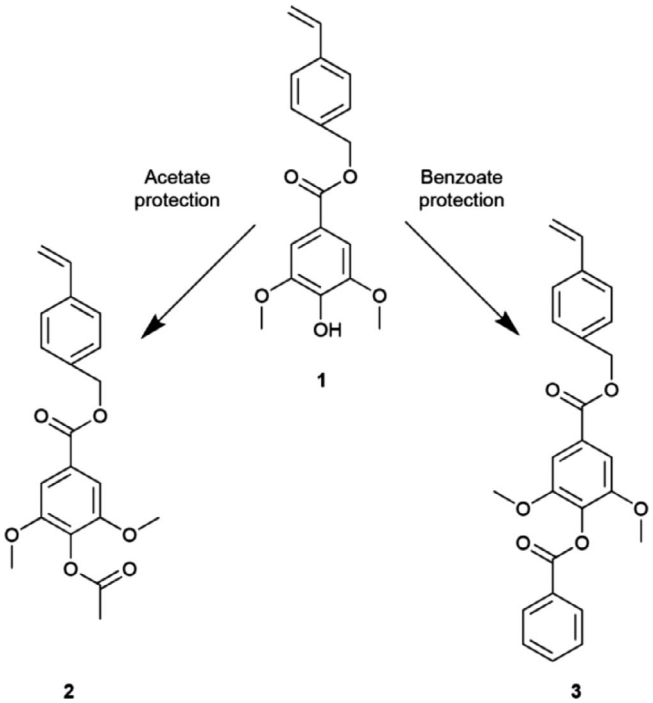

FIGURE 4 Protection of phenol group by acetic anhydride or benzoyl chloride, to yield compounds **2** and **3**.

TABLE 2 Compounds **2** and **3** free-radical polymerization molecular weight characterization. Polymerization of compound **3** yields high-molecular-weight polymer while compound **2** only produces small oligomers

Protecting group	Initiator	M_n (g.mol^{-1})	$Đ$
Acetate (**2**)	AIBN[a,c]	5,000	1.3
	ACCN[a,c]	4,500	1.3
	Benzoyl Peroxide[a,c]	4,700	1.3
	Dicumyl Peroxide[a,c]	4,700	4.7
Benzoate (**3**)	AIBN[a,c]	21,100	2.5
	ACCN[a,c]	25,300	3.8
	Benzoyl Peroxide[b,d]	1,100,000	3.0
	Dicumyl Peroxide[b,d]	790,000	1.2

[a] Bulk polymerization, 1%$_{mol}$ initiator.
[b] Bulk polymerization, 0.1%$_{mol}$ initiator.
[c] Performed in duplicates.
[d] Performed in triplicates.

Upon heating, the purified polymer showed high stability toward high temperature with a degradation temperature measured by TGA around 350°C. DSC indicated a clear T_g at 120°C (Fig. 7). Biopolymers with high thermal stability and processable properties are not widespread in industry. Compound **3** proves that aromatic biopolymers could become a platform for performant and high value added industrial polymer.

Functionalization through Phenol

The phenol radical scavenging properties hinder polymerization. However, protecting reaction decreases our overall bio-

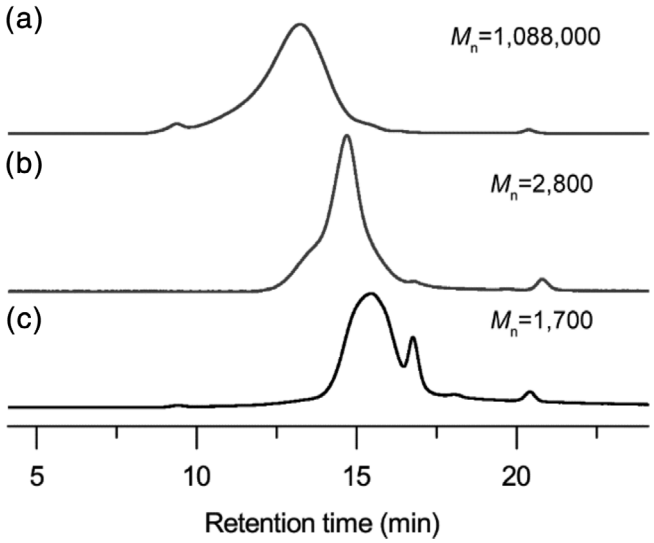

FIGURE 5 SEC analysis of the polymer synthesized by free-radical polymerization of (a) compound **3**, (b) compound **2**, and (c) compound **1**.

based content. By considering the phenol moieties instead of the carboxylic group for addition of alkene group both functionalization and protection are combined to increase efficiency. Methacryloyl chloride reacted with SA to yield compound **4** in high yield and high purity. Methacrylic anhydride was also considered as a greener alternative to methacrylic acid (74% bio-based). Atom economy is therefore reduced by side production of methacrylic acid (Fig. 8). Furthermore, complete purification is only achieved after intensive purification. However, as acid chloride requires energy intensive processes and involves toxic chemicals to be synthesized, the use of the anhydride is preferred.

Monomer **4** polymerized readily in aqueous solvent, while organic solvent only yielded low-molecular-weight oligomers (Table 3 and Supporting Information Table SI2). VA-086 proved to be the best initiator for solution polymerization with molecular weight up to M_n = 27,400 g.mol^{-1}. In reverse-emulsion conditions, AIBN initiator increased the final molecular weight up to 34,000 g.mol^{-1}. However, a simple aqueous polymerization is preferred as it offers a reduced waste process. TGA analysis of the obtained polymer indicated that thermal stability diminished compared to the polymer from compound **3**, with a degradation temperature of 300°C. The glass transition temperature was measured by DSC at T_g = 105°C (Fig. 9).

The high amount of free carboxylic acid functional group allowed the polymer from compound **4** to be water soluble. Future application such as post functionalization reaction can be considered in greener condition without the use of organic solvent.

CONCLUSIONS

Monomers from S-type lignin fragment were successfully synthesized from SA by two different functionalization strategies.

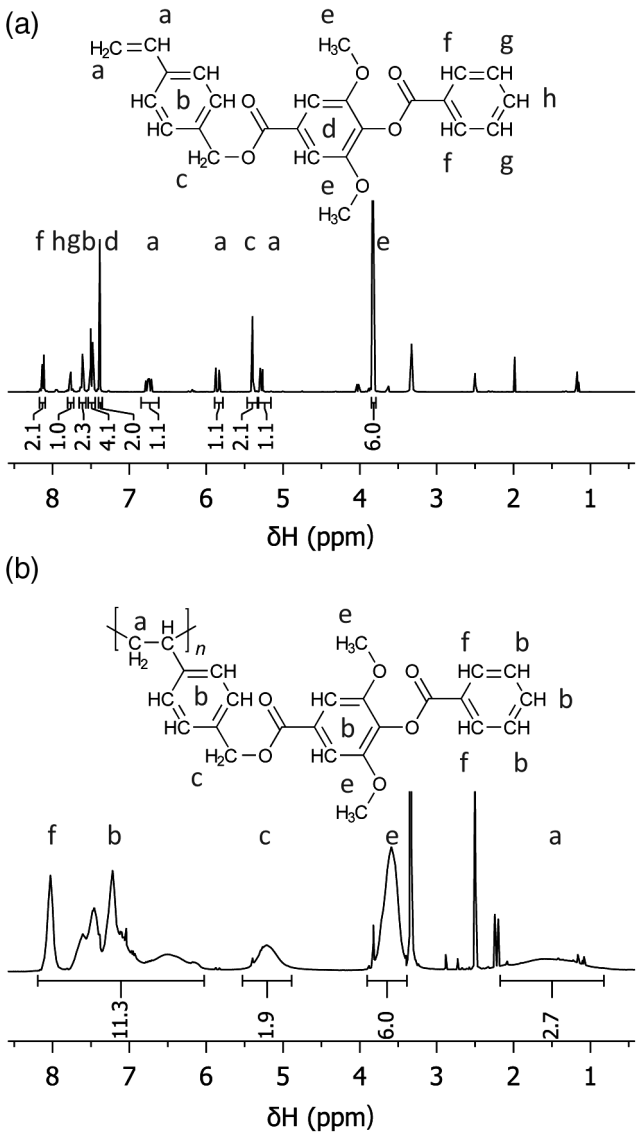

FIGURE 6 ^{1}H NMR in d6-DMSO analysis of (a) compound **3** and (b) polymer synthesized by free-radical polymerization.

Phenol moieties, although expected to be inactivated by steric hindrance from two neighboring methoxy group, exhibited intense anti-oxidant properties. This radical scavenging behavior proved to greatly hinder free-radical polymerization and the use of protecting group was required. Depending on the protection strategies, resulting polymer could be either obtained in high yield and low molecular weight (compound **2**), or super high molecular weight but low yield (compound **3**). The polymer was found to have great thermal stability and a glass transition temperature around 120°C.

A second functionalization strategies was designed in order to increase the overall bio-based material loading in the final product. As a result of free carboxylic acid group, a water soluble polymer was synthesized in organic-solvent free condition. The polymer glass transition temperature was found to

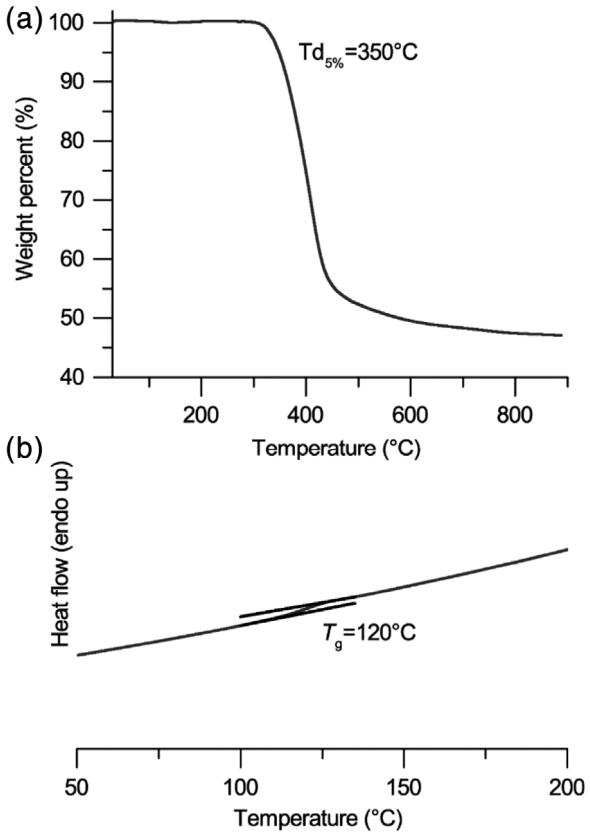

FIGURE 7 Polymerization of compound **3** yields a polymer with thermal stability higher than 350°C. High glass transition temperature is also detected by DSC.

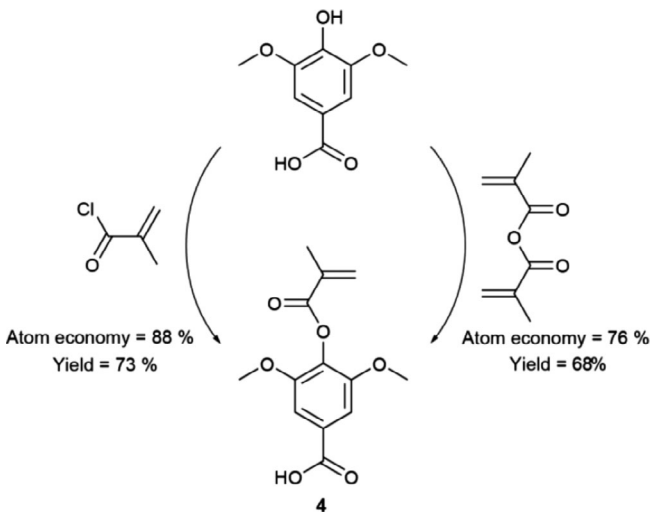

FIGURE 8 Synthesis of compound **4** can be achieved by methacryloyl chloride or methacrylic anhydride.

be very similar to polystyrene. It is clear that this biopolymer now offers a reliable green alternative for numerous application over a wide range of industries and is bound to witness a quick development in the future.

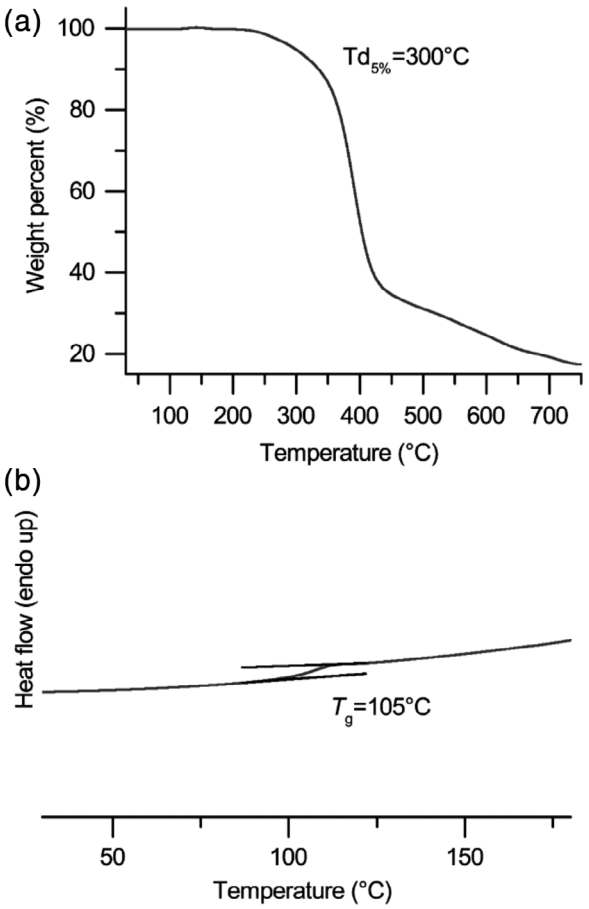

FIGURE 9 (a) Thermogravimetric analysis of polymer synthesized by free-radical polymerization of monomer **4** and (b) its glass transition temperature measured by differential scanning calorimetry.

TABLE 3 Free-radical polymerization of compound **4** in solvents and reverse emulsion conditions

Initiator	a[initiator]a / [monomer]	M_n (g/mol)	$Đ$
APS[a]	2%	10,400	3.2
AAPH[a]	2%	1,400	1.8
AIBN[a]	2%	1,500	2.1
VA-086[a]	2%	27,400	2.9
ACCN[a]	2%	3,400	2.3
tert-butyl peroxide[a]	2%	7,200	3.1
AIBN (reverse emulsion)[a]	2%	36,500	4.0
ACCN (reverse emulsion)[a]	2%	1,700	2.2

[a] Performed in duplicate.

EXPERIMENTAL SECTION

Chemicals and solvents: Chemicals were purchased from Sigma Aldrich (Sydney, NSW, Australia) (SA, vinyl benzyl chloride, pyridine, acetic anhydride, benzoyl chloride, 4-dimethylaminopyridine (DMAP), trimethylamine (TEA),

methacryloyl chloride, methacrylic anhydride, 2,2′-azobis(2-methylpropionitrile) (AIBN), 1,1′-azobis(cyclohexanecarbonitrile) (ACCN), dicumyl peroxide, benzoyl peroxide, ammonium persulfate (APS), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AAPH), sodium formaldehyde sulfoxylate, sodium dodecyl sulphate, span 80, lithium bromide), from Merck PTY (Melbourne, VIC, Australia) (Sodium bicarbonate, sodium nitrate, potassium phosphate monobasic, sodium chloride, anhydrous manganese sulphate, sodium hydroxide, deuterated chloroform, deuterium oxide, sodium deuteroxide), from TCI (Tokyo, Japan) (deuterated dimethyl sulfoxide or DMSO) and from FUJIFILM Wako Chemicals (Richmond, VA) (2,2′-azobis [2-methyl-*N*-(2-hydroxyethyl)propionamide] or VA-086) and used as received. Reagent grade solvents (anhydrous dimethylformamide or DMF, diethyl ether, hydrochloric acid, xylene, ethylene glycol, chloroform, toluene, methanol) were purchased from Thermo Fisher Scientific (Melbourne, VIC, Australia). PVA was synthesized by our group and had molecular weight of approximately 20,000 $g.mol^{-1}$.

The molecular weight of polymers samples was analyzed by SEC in DMF or water. SEC in DMF was performed at 40°C on a Tosoh EcosHLC-8320 equipped with double detectors (RI, UV 280 nm) using Tosoh alpha 4000 and 2000 columns. DMF/LiBr 0.1 M was used as a mobile phase (flow rate 1 mL/min). Polystyrene standards were used for the calibration. Similarly, aqueous SEC was performed on a Tosoh EcosHLC-8320 equipped with double detectors (RI, UV 305 nm) using three TSKgel PWXL columns (TSKgel G5000PWxL, TSKgel G6000PWxL, and TSKgel MPWxL) connected in series. The mobile phase solution was prepared by mixing sodium nitrate and sodium bicarbonate (0.1M $NaNO_3$ 0.1M $NaHCO_3$), and the flow rate was set to 1 mL/min. Polyacrylic acid standards were used for calibration.

^1H experiments were performed in deuterated DMSO on a Bruker Avance 400 MHz NMR spectrometer equipped with a CryoProbe Prodigy 5 mm $^1H/^1H$-$^{13}C/^{15}N$ probe. NMR experiments were performed with the sample held at 25 ± 0.1°C. Chemical shifts for all experiments are referenced using the Unified Scale relative to 0.3% tetramethylsilane in deuterated chloroform.[24,25]

Degradation temperatures were measured by TGA performed on a Simultaneous Thermal Analyzer (STA) 8000 from PerkinElmer. Heating rate was fixed to 30°C/min under nitrogen flow.

Glass transition temperatures were measured by DSC on a DSC 8000 from PerkinElmer fitted with a dual-stage heat-exchanger cooling system Intracooler 2. Samples were analyzed in aluminum pans and under nitrogen atmosphere. The heating rate was set to 10°C/min and cooling rate 150°C/min.

An Agilent Technologies Cary 630 FTIR was used for IR spectrum acquisition. Data analysis was carried on Respro software.

Mass analysis was coupled with LC-UV equipment with the following parameters. An Agilent 1260 Infinity liquid chromatograph system was coupled with 6120 series quadrupole mass spectrometer. A Kinetex 5 μm C18 100 Å column (250 mm × 4.6 mm ID particle size 5 μm) was used with 0.2% HCOOH in water and 0.2% HCOOH in acetonitrile as gradient of mobile phase (0.8 mL/min) maintained at 30°C. Mass parameters were set as follow: drying gas flow of 9.8 L/min, nebulizer pressure of 28 psi, drying gas temperature of 300°C, and capillary voltage of 3000 V. Mass scan range was set to 100–900 Da with a cycle time of 1.57 sec per cycle.

Compound 1 Synthesis

Functionalization of SA by vinyl benzyl chloride was conducted in anhydrous DMF. Ten grams of SA (50.5 mmol) were added in a dried round-bottom flask to 5.35 g of anhydrous sodium carbonate (50.5 mmol) along with the solvent (50 mL). After few minute of stirring and N_2 flushing, vinyl benzyl chloride (0.7 mL, 5.05 mmol) was added slowly through a septum. After addition, the solution was heated at 60°C and let to react overnight. For work up, the reaction mixture was allowed to cool down. One hundred fifty milliliters of water were added to the solution, which was then extracted five times with 30 mL of diethyl ether. The combined organic phases were then washed successively with water (30 mL, three times) and brine (30 mL). After drying on $MgSO_4$, the organic phase was evaporated to yield compound **1**, yield 52%. More than 95% of unreacted SA could be recovered by acidification and filtration of aqueous phase to be reused in future reactions. ^1H-NMR (400 MHz, d6-DMSO): δ 7.49 (d, 2H, ArH), δ 7.44 (d, 2H, ArH), δ 7.24 (s, 2H, ArH), 6.73 (m, H, HC=), 5.86 (d, H, H_2C=), 5.31 (s, 2H, CH_2), 5.26 (d, H, H_2C=), 3.81 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, d6-DMSO): δ 166 (OO-C-Ar), δ 148 (Ar), δ 138 (Ar), δ 134 (Ar), δ 129 (Ar), δ 126 (Ar), δ 114 (Ar-CH=), δ 108 (CH_2=), δ 67 (Ar-CH_2-O), δ 56 (O-C-H_3). IR (KBr): ν_{O-H} = 3432 cm^{-1}, ν_{Ar-H} = 3077 cm^{-1}, ν = $_{C-H}$ = 3059 cm^{-1}, ν_{C-H} = 2950 cm^{-1}, $\nu_{C=O}$ = 1746 cm^{-1}, $\nu_{C=C}$ = 1674 cm^{-1}, ν_{Ar-Ar} = 1602 cm^{-1}, ν_{C-H} = 1473 cm^{-1}, ν_{C-H} = 1369 cm^{-1}, ν_{C-O} = 1254 cm^{-1}, ν_{C-O} = 1137 cm^{-1}. m/z: 314.0 (6.3%), 199.0 (13.5%), 181.0 (19.5%), 153.0 (100.0%), 131.0 (12.4%), 117.0 (25.8%), 103.0 (7.7%), 43.0 (14.5%).

Compounds 2 and 3 Synthesis

Protection of compound **1** (5 g, 15.8 mmol) by acetate group was conducted in anhydrous pyridine (50 mL). After flushing for about 15 min with nitrogen acetic anhydride (1.8 mL, 19.11 mmol) was added through a septum. Heating was set to achieve reflux and solution was let to react overnight. After cool-down 200 mL of diethyl ether was added, and the organic phase was washed successively with 1 M HCl (three times, 100 mL), 1 M NaOH (three times, 100 mL), and brine (150 mL). After drying on $MgSO_4$, solvent was evaporated under reduced pressure to yield compound **2** in high yield (>99%). 1H-NMR (400 MHz, d6-DMSO): δ 7.50 (d, 2H, ArH), δ 7.40 (d, 2H, ArH), δ 7.33 (s, 2H, ArH), 6.79 (m, H, HC=), 5.87 (d, H, H2C=), 5.38 (s, 2H, CH2), 5.27 (d, H, H2C=), 3.83 (s, 6H, CH3), 2.29 (s, 3H, OOCCH3). 13C-NMR (100 MHz, d6-DMSO): δ 172 (ArOO-C-CH3), δ 167 (OO-C-Ar), δ 152 (Ar), δ 137 (Ar), δ 136 (Ar), δ 133 (Ar), δ 128 (Ar), δ 126 (Ar), δ 115 (Ar-CH=), δ 108 (CH2=), δ 69 (Ar-CH2-O), δ 59 (O-C-H3), δ 21 (OOC-

CH3). IR (KBr): νAr-H = 3053 cm − 1, ν = C-H = 3064 cm − 1, νC-H = 2943 cm − 1, νC-H = 2932 cm − 1, νC = o = 1758 cm − 1, νC=C = 1673 cm − 1, νAr-Ar = 1662 cm − 1, νC-H = 1488 cm − 1, νC-H = 1357 cm − 1, νC-o = 1243 cm − 1, νC-o = 1173 cm − 1. m/z: 314.0 (6.3%), 241.0(19.6%), 223.0 (23.3%), 195.0 (100%), 131.0 (14.1%), 117.0 (16.7%), 103.0 (6.5%), 43.0 (34.3%).

Similarly, protection by benzoate group was performed in anhydrous pyridine. Compound **1** (5,0 g, 15.8 mmol) was dissolved in pyridine (50 mL), while flushing for about 15 min with nitrogen. Reaction flask was maintained on ice while benzoyl chloride (2.2 mL, 18.9 mmol) was slowly added through a septum. The reaction was maintained on ice for 1 h, then allowed to continue at room temperature (RT) for a further 4 h. Two hundred milliliters of diethyl ether was then added to the flask, and the solution was washed successively with 1 M HCl (three times, 100 mL), 1 M NaOH (three times, 100 mL), and brine (150 mL). After drying on $MgSO_4$, the solvent was evaporated under reduced pressure to yield compound **3** in high 90% yield. ^{1}H-NMR (400 MHz, d6-DMSO): δ 8.11 (d, 2H, ArH), δ 7.77 (t, H, ArH), δ 7.61 (d, 2H, ArH), δ 7.48 (d, 4H, ArH), δ 7.38 (s, 2H, ArH), 6.76 (m, H, HC=), 5.88 (d, H, H_2C=), 5.40 (s, 2H, CH_2), 5.27 (d, H, H_2C=), 3.83 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, d6-DMSO δ 168 (OO-C-Ar), δ 163 (ArOO-C-Ar), δ 152 (Ar), δ 138 (Ar), δ 136 (Ar), δ 133 (Ar), δ 130 (Ar), δ 129 (Ar), δ 128 (Ar), δ 127 (Ar), δ 116 (Ar-CH=), δ 107 (CH_2=), δ 67 (Ar-CH_2-O), δ 56 (O-C-H_3). IR (KBr): $\nu_{Ar\text{-}H}$ = 3073 cm^{-1}, $\nu_{=C\text{-}H}$ = 3058 cm^{-1}, $\nu_{C\text{-}H}$ = 2957 cm^{-1}, $\nu_{C=O}$ = 1763 cm − 1, $\nu_{C=C}$ = 1622 cm^{-1}, $\nu_{Ar\text{-}Ar}$ = 1675 cm^{-1}, $\nu_{C\text{-}H}$ = 1493 cm^{-1}, $\nu_{C\text{-}H}$ = 1335 cm^{-1}, $\nu_{C\text{-}O}$ = 1242 cm^{-1}, $\nu_{C\text{-}O}$ = 1178 cm^{-1}. m/z: 314.0 (8.9%), 303.0 (26.7%), 285.0 (23.4%), 257.0 (100%), 131.0 (17.1%), 117.0 (23.8%), 103.0 (8.2%), 43.0 (5.4%).

Compound 4 Synthesis

SA (10.0 g, 50.5 mmol) was added in anhydrous DMF (50 mL), along with TEA (17.5 mL, 0.125 mol) and DMAP (616 mg, 5.05 mmol) and stirred until complete dissolution. The reaction mixture was then kept on ice and flushed with nitrogen for 1 h. Methacryloyl chloride (4.5 mL, 46.1 mmol) was carefully and slowly added through a septum over ~20 min. The reaction mixture was further kept on ice for 3 h, and then let overnight at room temperature. Five hundred milliliters of water were added to the mixture at the end of the reaction, and extracted five times with 50 mL of chloroform fractions. The combined organic phases were then washed with pH = 6 buffer solution (five times, 50 mL), 1 M HCl (50 mL), and brine (50 mL) successively. Organic phase was then dried on $MgSO_4$, and solvent was removed under reduced pressure. Compound **4** was obtained with 73% yield. ^{1}H-NMR (400 MHz, d6-DMSO): 7.30 (s, 2H, ArH), 6.28 (s, H, H_2C=), 5.91 (s, H, H_2C=), 3.81 (s, 6H, OCH_3), 1.99 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, d6-DMSO): δ 166 (OO-C-Ar), 148 (Ar), 138 (Ar), 134 (Ar), 129 (Ar), 126 (Ar), 114 (Ar-CH=), 108 (CH_2=), 67 (Ar-CH_2-O), 56 (O-C-H_3). IR (KBr): $\nu_{O\text{-}H}$ = 3598 cm^{-1}, $\nu_{Ar\text{-}H}$ = 3023 cm^{-1}, ν = $_{C\text{-}H}$ = 3084 cm^{-1}, $\nu_{C\text{-}H}$ = 2943 cm^{-1}, $\nu_{C\text{-}H}$ = 2926 cm^{-1}, $\nu_{C=O}$ = 1743 cm^{-1}, $\nu_{C=C}$ = 1645 cm^{-1}, $\nu_{Ar\text{-}Ar}$ = 1595 cm^{-1}, $\nu_{C\text{-}H}$ = 1474 cm^{-1}, $\nu_{C\text{-}H}$ = 1401 cm^{-1}, $\nu_{C\text{-}O}$ = 1234 cm^{-1}, $\nu_{C\text{-}O}$ = 1269 cm^{-1}. m/z: 249.0 (13.7%), 221.0 (35.9%), 198.0 (100%), 69.0 (43.5%), 43.0 (23.6%).

Alternatively, compound **4** can be obtained by the addition of methacrylic anhydride to SA. SA (10.0 g, 50.5 mmol) was dissolved in anhydrous DMF (50 mL) along with DMAP (123 mg, 1.01 mmol). The reaction mixture was flushed with nitrogen for about 1 h. Methacrylic anhydride (11.3 mL, 75.7 mmol) was added through a septum, and the solution was stirred for 1 h at room temperature before increasing heating to 50°C and allowing the reaction to proceed overnight. After cooldown, water and chloroform were added in the reaction flask. The organic phase was collected and the aqueous phase was further extracted four times. All organic phases were combined and washed five times with pH = 6 buffer, 1 M HCl, and brine successively. The organic phase was then dried on $MgSO_4$ and the solvent removed under reduced pressure. Compound **3** was obtained with 68% yield.

Polymerization of Compounds 1, 2, 3, and 4

Radical polymerizations in bulk or organic solvent were conducted in the following conditions. Monomer was dissolved in solvent (if any) at concentration 0.4 M.L^{-1} then heated to polymerization temperature: 70°C (AIBN), 90°C (ACCN), 110°C (benzoyl peroxide) or 140°C (dicumyl peroxide). Finally, the initiator was added to the reaction and heating was maintained for 6 h. After cool down reaction mixture was added dropwise to acetone or diethyl ether to crush out and recover the polymer. Polymerizations experiment were done in duplicates or triplicates (Table 2).

For emulsion polymerization, the monomer was dissolved in toluene or xylene. PVA and sodium dodecyl sulfate (10%$_{w/w}$ to monomer each) were then added and mixed well with a small amount of water, while bubbling nitrogen for about 15 min. Finally, initiators were added and heating was turned on as required. After 6 h, the reaction mixture was collected and crushed out in acetone to recover the polymer.

Aqueous polymerization for compound 4 was conducted in alkaline condition (NaOH/compound **3** = 1:1 molar ratio). Nitrogen was bubbled for about 15 min. Heating was set to polymerization temperature and initiator were added to reaction: APS (80°C), AAPH (80°C), AIBN (80°C), VA-086 (90°C), and *tert*-butyl hydroperoxide (95°C). After 6 h, solution was collected and purified by dialysis on Snakeskin molecular weight cut off 3,000 Da. The remaining product was then isolated by lyophilisation. Polymerizations experiment were done in duplicates (Table 3).

Reverse emulsion polymerization was performed by dissolving the monomer in alkaline solution (NaOH/compound **3** = 1:1 molar). The monomer solution was then added dropwise in a vigorously stirred solution of toluene and PVA plus span 80 (10%$_{w/w}$ to monomer each). Finally, heating was turned on. After about 6 h reaction, the mixture was collected and crushed out in acetone to recover the polymer. Polymerizations experiment were done in duplicates (Table 3).

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