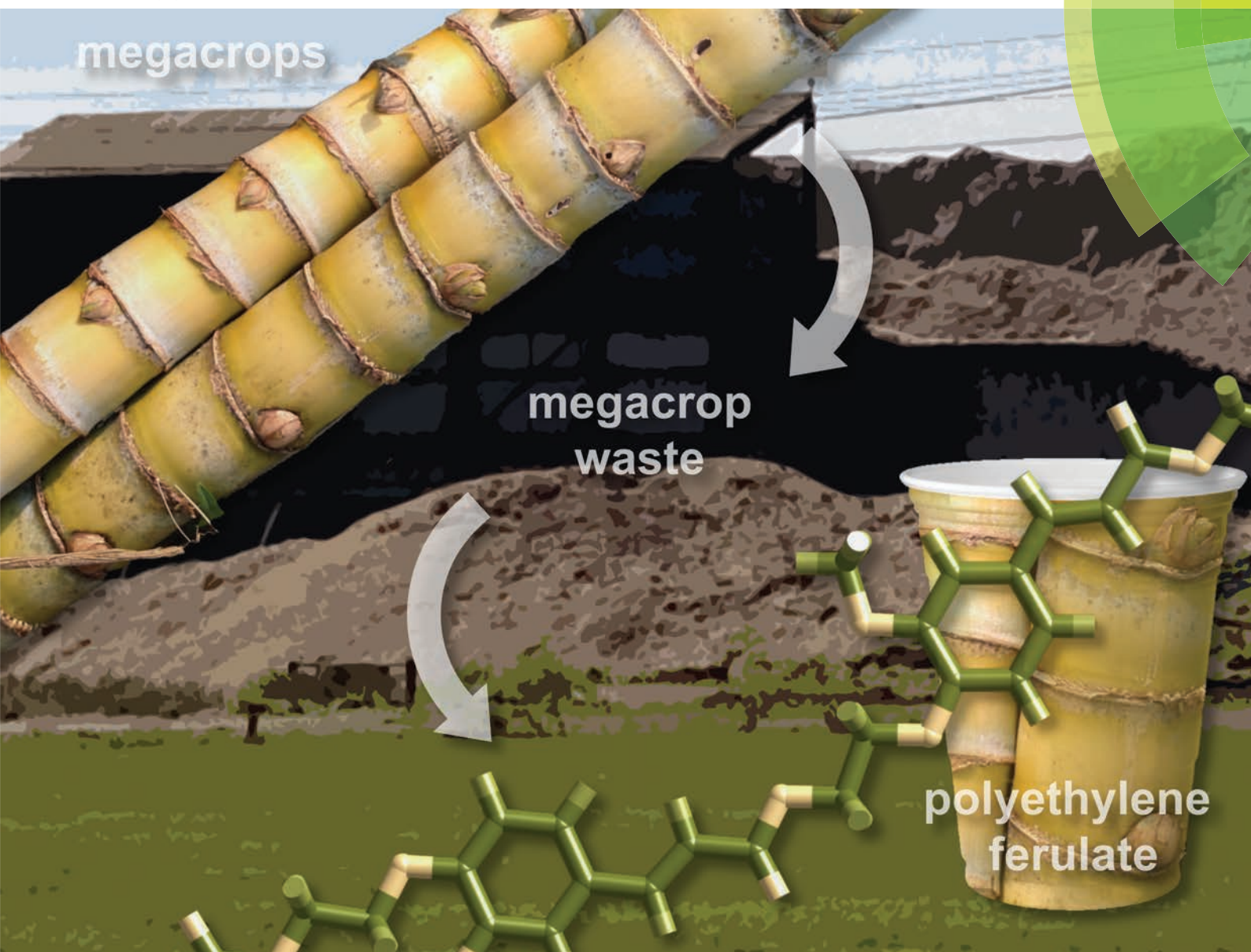


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Polyethylene ferulate (PEF) and congeners: polystyrene mimics derived from biorenewable aromatics†

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Ferulic acid and *p*-coumaric acid are abundant, biorenewable precursors for the synthesis of polyethylene ferulate (PEF) and polyethylene coumarate (PEC), as well as cognate copolymers with prescribed hydrogenation of the main-chain double bond. By controlling the comonomer feed ratios, copolymers with tunable thermal properties are obtained, including the thermal range occupied by polystyrene (PS).

Worldwide, polystyrene (PS) is one of the most popular commodity plastics, accounting for about 9% of the global plastic market.¹ This hydrocarbon polymer with aromatic side groups is synthesized from styrene, a monomer wholly derived from non-renewable fossil fuels (Fig. 1). Despite its broad utility as a packaging plastic, polystyrene is neither biorenewable nor biodegradable and persists in the environment long after its use. It has been realized that unreacted styrene monomer can remain in the polymer and is continually released throughout the PS life cycle.² This situation is potentially calamitous because styrene has been reported as a hazardous air pollutant³ and a human carcinogen.⁴ For this reason, polystyrene containers (*e.g.*, cups and food packaging) can potentially

threaten human health after prolonged exposure. Even though polystyrene is recycled in some regions (*e.g.*, Europe), most is either discarded into landfills or directly into the open environment, often concentrating in rivers and oceans—especially for foamed polystyrene, which floats.

Contrasting the positive material advantages of PS against its negative environmental impact, we have sought to develop new classes of environmentally compatible polystyrene mimics. These should be sourced from plants instead of toxic, fossil fuel feedstocks and they should degrade with greater facility in natural environments, leaving behind benign by-products.

The optimal source for renewable aromatics is lignin, which makes up about 30% of biomass and is the second most abundant organic polymer on earth.⁵ Ferulic acid (FA) and *p*-coumaric acid (CA) are the two most abundant hydroxycinnamic acids in the plant kingdom^{6,7} and these can be sourced from lignin and, especially, the lignocellulose of megacrops sugarcane and corn. Not only are these aromatic acids abundantly available from non-food agricultural waste (bagasse, stover), they possess antioxidant properties which protect against oxidative stress in cells and the progression of age-related diseases,⁸ as well as reduce the risk of some types of cancer.^{9–12} Present in virtually all plants, these hydroxycinnamic acids are especially abundant in “superfoods”.

In 2010, our group reported the synthesis of polydihydroferulic acid (PHFA), a polyethylene terephthalate (PET) mimic made from either vanillin or ferulic acid building blocks (Fig. 2).¹³ An important revelation was the necessity of flexible segments along the polymer backbone. Polyferulic acid itself (PFA) is an insoluble, intractable material with a melting temperature (T_m) of 325 °C and a glass transition temperature (T_g) of 150 °C.¹⁴ These high values predict poor processability, especially as the T_m approaches the decomposition temperature. In the case of its hydrogenated analogue, PHFA, the two sp^3 carbons in the main chain suitably reduce the melting temperature to 234 °C, but still allow for a T_g (73 °C) to compete with that of PET (67 °C). While a T_g of 73 °C is a laudable achievement for a renewable thermoplastic polyester,

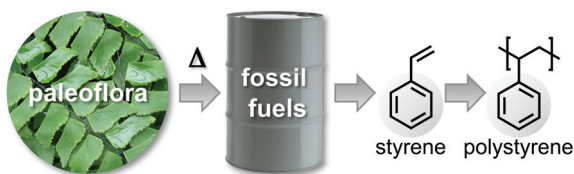


Fig. 1 The aromatic component of polystyrene (PS) confers desirable thermal properties, but PS is wholly derived from non-renewable fossil fuel feedstocks and has poor degradation behaviour.

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† Electronic supplementary information (ESI) available: Synthetic details, complete polymer characterization data, and method to determine copolymer composition. See DOI: 10.1039/c5gc01104c

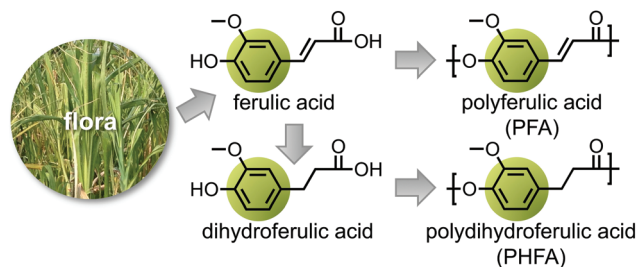


Fig. 2 Polydihydroferulic acid (PHFA), with main chain saturation, is a more tractable variant of polyferulic acid (PFA).

values matching those of PS, near 95 to 100 °C,¹⁵ would constitute an additional achievement.

Herein, we reveal our subsequent pursuits of crafting renewable polymers, with improved thermal properties, from hydroxycinnamic acids. The hydrogenation of the double bond in ferulic acid or *p*-coumaric acid is one approach for incorporating the necessary conformational flexibility into the polymer main chain. An alternative strategy is to leave the double bond intact and install sp^3 hybridized carbons elsewhere. Thus, monomers were synthesized by appending alkylene spacers of various lengths to ferulic acid and *p*-coumaric acid by reaction with chloroalkylene alcohols (Scheme 1) *via* adaptation of literature procedures.¹⁶ Additional saturation and flexibility were introduced by subsequent hydrogenation of hydroxyethylferulic acid ($n = 2$) and hydroxyethylcoumaric acid ($n = 2$), affording hydroxyethyldihydroferulic acid and hydroxyethyldihydrocoumaric acid monomers, respectively.

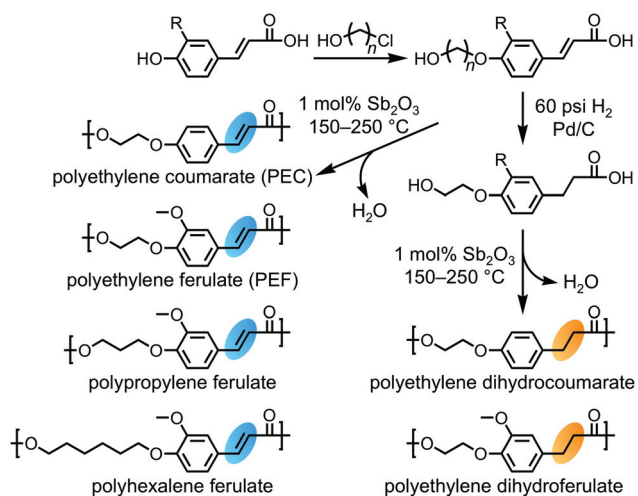
Once the monomers were obtained, homopolymerizations were conducted using 1 mol% of Sb_2O_3 catalyst. Following a temperature ramp, typically from 150 to 250 °C over a period of 4 hours under an atmosphere of argon, the reactions were

subjected to dynamic vacuum for 8 hours in order to eliminate the by-product water generated from the step-growth reaction, thus driving the polymerization. All the polymerizations were performed in the dark by covering the apparatus with aluminum foil to avoid unwanted photochemical reactions.¹⁷ As shown in Table 1, the six homopolymers were obtained in excellent yields (85.9 to 93.1%) with appreciable molecular weights. M_n values ranged from 1600 to 22 900 and the polydispersity index (PDI) values were somewhat typical for step-growth polymerizations, ranging from 1.6 to 3.6. The homopolymers showed good thermal stability, exhibiting a 50% mass loss under nitrogen at temperatures from 394 to 536 °C.

Sasiwilaskorn *et al.*¹⁸ explored the synthesis of polyethylene coumarate (PEC) homopolymer (*cf.*, Table 1, entry 3) using *N*, *N*-dicyclohexylcarbodiimide (DCC) as a coupling agent, but the polymer was impure with no reported thermal properties or molecular weight characterization. Hydroxyethylcoumaric methylester has been investigated as a comonomer for photocrosslinkable polymers.¹⁹ A patent from 1998 reported polypropylene ferulate (*cf.*, Table 1, entry 5) synthesis for producing phase retarder films, but thermal properties and molecular weights were not reported.²⁰ Meier *et al.*²¹ discovered polycondensation of hydroxyethyldihydroferulic methylester to form polyethylene dihydroferulate (*cf.*, Table 1, entry 2) using triazabicyclodecene (TBD) as an organocatalyst. However, our direct polycondensation from hydroxyethyldihydroferulic acid using Sb_2O_3 as the catalyst gave a significantly higher molecular weight ($M_n = 22\,100$ vs. 5440) and a higher glass transition temperature ($T_g = 32$ °C vs. -27 °C).

As recorded in Table 1, the polyalkylene hydroxycinnamates and polyalkylene dihydrohydroxycinnamates exhibited different thermal behaviours depending on the number of methylene spacers, the presence of aromatic methoxy substituents, and the unsaturation or saturation of the α and β carbons. For the three polyalkylene ferulate polymers, the glass transition temperature decreased significantly with an increase in the number of methylene groups; $T_g = 113$ °C for $n = 2$, 82 °C for $n = 3$, and 51 °C for $n = 6$, (Table 1, entries 1, 5, and 6, respectively). The aromatic methoxy substituent had a minimal effect on the T_g . Polyethylene ferulate (PEF, Table 1, entry 1), with an aromatic methoxy group, showed a glass transition temperature (113 °C) merely 4 degrees greater than that of polyethylene coumarate (109 °C, PEC, Table 1, entry 3), having no methoxy group. The hydrogenated analogues compared similarly; polyethylene dihydroferulate (32 °C, Table 1, entry 2) showed a glass transition temperature merely 8 degrees greater than that of polyethylene dihydrocoumarate (24 °C, Table 1, entry 4). Comparison of polyethylene ferulate with its hydrogenated analogue reveals a precipitous drop in the T_g : $\Delta = 81$ °C = 113 °C–32 °C (Table 1, entries 1 and 2). Likewise, comparison of polyethylene coumarate with its hydrogenated analogue reveals an abrupt drop in the T_g : $\Delta = 85$ °C = 109 °C–24 °C (Table 1, entries 3 and 4).

Overall, the effect of polymer structure on the glass transition temperature follows reasonable predictions. As the polymers acquire more conformational flexibility with larger n or



Scheme 1 Synthetic route from coumaric acid ($R = H$) and ferulic acid ($R = OMe$) to polyalkylene hydroxycinnamates (blue, left) and polyalkylene dihydrohydroxycinnamates (orange, right).

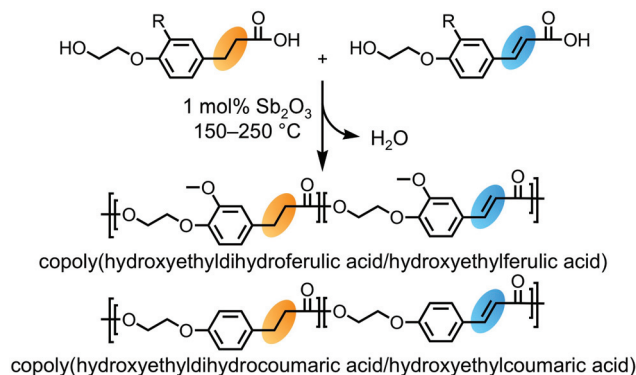
Table 1 Homopolymerization results and characterization of polyalkylene hydroxycinnamates and polyalkylene dihydrohydroxycinnamates^a

Entry	Polymers	Yield (%)	M_n^b (Da)	M_w^b (Da)	PDI ^b	T_g^c (°C)	T_m^c (°C)	$T_{50\%}^d$ (°C)
1		89.6	1600	2500	1.6	113	n.o.	536
2		87.1	22 100	79 400	3.6	32	n.o.	394
3		85.9	— ^e	— ^e	— ^e	109	n.o.	433
4		90.5	22 900	63 400	2.8	24	123	415
5		93.1	7700	13 700	1.8	82	n.o.	405
6		92.7	10 000	26 600	2.6	51	n.o.	397

^a 1 mol% Sb₂O₃; mixtures were typically melted under argon during a 4 hour temperature ramp from 150 to 250 °C; 8 hours of dynamic vacuum at 250 °C. ^b Obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. ^c Determined by DSC, n.o. = not observed. ^d Temperature at which 50% mass loss is observed under nitrogen. ^e Insolubility of the polymer prevented GPC analysis.

double bond saturation (a greater fraction of sp³ vs. sp² carbons), lower temperatures suffice to effect long-range chain motions. And, while the effect is smaller, a methoxy group increases the conformational barriers for chain motion, increasing the T_g . Incidentally, polymer solubility also tracked with polymer flexibility. Gel permeation chromatography (GPC) analysis of the most rigid polymers gave small (Table 1, entries 1 and 5) or absent (Table 1, entry 3) peaks—suggesting that insolubility may belie the real molecular weights. The most flexible polymers (Table 1, entries 2, 4, and 6) were easily solubilized in the GPC solvent, hexafluoroisopropanol (HFIP), gave larger GPC signals, and showed higher molecular weights (M_n between 10 000 and 22 900). For all six homopolymers, only polyethylene dihydrocoumarate (Table 1, entry 4) exhibited a melting temperature, which was measured at 123 °C. It seems the other five polymers resist crystallite formation under the conditions tested.

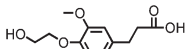
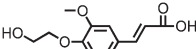
A copolymerization strategy was implemented to tune the degree of saturation in the polymer main chain which, in turn, should modulate the glass transition temperature.²² As described in Scheme 2, copoly(hydroxyethyl dihydroferulic acid/hydroxyethyl ferulic acid) (R = OMe) and copoly(hydroxyethyl dihydrocoumaric acid/hydroxyethyl coumaric acid) (R = H) copolymers can be synthesized with 1 mol% of Sb₂O₃ catalyst under the same conditions that functioned for the homopolymerizations. As tabulated in Table 2, ¹H NMR spectroscopy confirmed that the incorporation fraction closely matched the feed fraction for these copolymerizations. The copolymers were obtained in high yields (76.4 to 94.1%) and M_n values

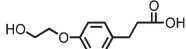
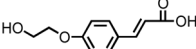
**Scheme 2** Synthetic route to copoly(hydroxyethyl dihydroferulic acid/hydroxyethyl ferulic acid) (R = OMe) and copoly(hydroxyethyl dihydrocoumaric acid/hydroxyethyl coumaric acid) (R = H).

ranged from 1600 to 39 000 with half of the samples above M_n = 10 900. The lower molecular weights (Table 2, entries 6–11) correlated with polymer rigidity (greater unsaturation) and may simply be a result of poor solubility in the GPC solvent (HFIP). The two polymers with the greatest hydroxyethylcoumaric acid content (Table 2, entries 15 and 16) were completely insoluble in HFIP. A few of the samples show uncharacteristically high PDI values, but most were in the typical range for a step-growth polymerization (1.5 to 3.1).

An additional investigation of these peculiar molecular weights was conducted by tracking the GPC behaviour and

Table 2 Polymerization results and characterization of copolymers prepared according to Scheme 2^a

Entry	Monomer feed (%)		Inc. FA ^b (mol%)	Yield (%)	M_n^c (Da)	M_w^c (Da)	PDI ^c	T_g^d (°C)	$T_{g\text{ Fox}}^e$ (°C)	$T_{50\%}^f$ (°C)
										
1	100	0	0	87.1	22 100	79 400	3.6	32	32	394
2	90	10	12	91.7	39 000	228,700	5.9	37	38	388
3	80	20	19	88.4	26 500	81 100	3.1	41	45	389
4	70	30	27	89.5	22 800	60 400	2.7	46	53	385
5	60	40	37	90.9	12 900	25 000	1.9	52	60	386
6	50	50	53	90.9	5700	16 900	3.0	58	67	392
7	40	60	56	76.4	5900	11 100	1.9	66	75	389
8	30	70	66	82.5	3400	6400	1.9	77	84	396
9	20	80	74	89.9	3200	6000	1.9	87	93	414
10	10	90	84	90.6	1900	2900	1.5	98	102	441
11	0	100	100	89.6	1600	2500	1.6	113	113	356

Entry	Monomer feed (%)		Inc. CA ^b (mol%)	Yield (%)	M_n^c (Da)	M_w^c (Da)	PDI ^c	T_g^d (°C)	$T_{g\text{ Fox}}^e$ (°C)	$T_{50\%}^f$ (°C)
										
12	100	0	0	90.5	22 900	63 400	2.8	24	24	415
13	90	10	10	92.2	29 400	134 500	4.6	29	31	415
14	50	50	51	94.1	10 900	40 500	3.7	56	61	418
15	10	90	92	87.3	— ^g	— ^g	— ^g	94	98	430
16	0	100	100	85.9	— ^g	— ^g	— ^g	109	109	433

^a 1 mol% Sb₂O₃; mixtures were typically melted under argon during a 4 hour temperature ramp from 150 to 250 °C; 8 hours of dynamic vacuum at 250 °C. ^b Incorporation of hydroxyethylferulic acid (hydroxyethyl FA) and hydroxyethylcoumaric acid (hydroxyethyl CA) in the copolymers determined by ¹H NMR. ^c Obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. ^d Determined by DSC. ^e Calculated using the Fox equation. ^f Temperature at which 50% mass loss is observed under nitrogen. ^g Insolubility of the polymers prevented GPC analysis.

glass transition temperature as a function of the polymerization time. Thus, eight aliquots were removed during an eleven hour copolymerization of hydroxyethyldihydroferulic acid and hydroxyethylferulic acid (in a 30:70 ratio, akin to Table 2, entry 8) with a temperature ramp from 180 °C to 240 °C (see the ESI†). After one hour, only oligomers were observed, with M_n = 400 and M_w = 870. Over the next 10 hours, molecular weight increased and then seemingly decreased with a maximum M_n of 5900 for T_p = 5 hours. We attribute the apparent molecular weight reduction to an artifact of the GPC analysis because of insolubility in HFIP. Corroborating evidence is the unwavering rise in the glass transition temperature over time, with measured T_g values progressing as expected for a step-growth polymerization: 42, 63, 66, 69, 72, 73, 74, and 77 °C.

Fig. 3 illustrates the fine control possible over the glass transition temperature of the copolymers. As predicted by the Fox equation,²³ the glass transition temperatures followed a proportional increase as the unsaturated monomer content increased, reaching a maximum with 100% unsaturated monomer fraction. Thus, a steady increase in the T_g is possible by increasing the feed fraction of the unsaturated comonomer. For the ferulic acid-based copolymers (R = OMe), the T_g range is 32 °C to 113 °C and the 50:50 (feed) copolymer has a T_g of 58 °C (Table 2, entry 6). The 10:90 (feed) copolymer exhibits a

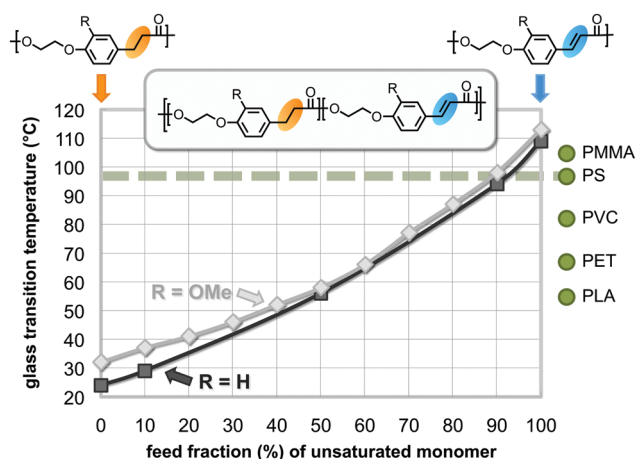


Fig. 3 Glass transition temperatures observed and plotted for copoly (hydroxyethyldihydroferulic acid/hydroxyethylferulic acid) (R = OMe, light grey diamonds) and copoly(hydroxyethyldihydrocoumaric acid/hydroxyethylcoumaric acid) (R = H, dark grey squares).

T_g of 98 °C, which is the targeted match of the T_g for polystyrene. For the coumaric acid-based copolymers (R = H), the T_g range is slightly lower from 24 °C to 109 °C and the 50:50 (feed) copolymer has a T_g of 56 °C (Table 2, entry 14). The

10 : 90 (feed) copolymer exhibits a T_g of 94 °C, which is essentially the targeted match of the T_g for polystyrene. Note that the T_g range of these two copolymers spans the T_g values of several common commodity plastics, from polylactic acid (PLA, 55 °C) to polyethylene terephthalate (PET, 67 °C) to polyvinyl chloride (PVC, 82 °C) to polystyrene (PS, 95–100 °C) to polymethyl methacrylate (PMMA, 105 °C).

Conclusions

Because chain structure and flexibility are paramount to polymeric thermal properties, the naturally abundant phytochemicals ferulic acid and *p*-coumaric acid have been converted into four targeted monomers with varying degrees of conformational freedom: (1) hydroxyethylferulic acid, (2) hydroxyethyldihydroferulic acid, (3) hydroxyethylcoumaric acid, and (4) hydroxyethyldihydrocoumaric acid. The homopolymerizations and copolymerizations of these monomers yield a novel family of biorenewable thermoplastics with programmable glass transition temperatures (T_g). For example, the polyethylene ferulate (PEF) homopolymer exhibited a T_g of 113 °C and the polyethylene dihydroferulate homopolymer exhibited a T_g of 32 °C. The corresponding copolymer series spanned the full range of intermediate T_g values, matching those of several high-volume commodity polymers. Importantly, the ferulic acid-based copolymer with a 10 : 90 feed ratio (predominantly composed of hydroxyethylferulic acid with 10% of the hydrogenated congener) exhibited a T_g of 98 °C, an excellent match for the T_g of polystyrene (PS). Similarly, the 10 : 90 coumaric acid-based copolymer showed a T_g of 94 °C, suggesting that it could also serve as a PS mimic.

These polyalkylene hydroxycinnamates revealed important structure/property relationships, including: a significant decrease in the T_g with an increasing number of methylene groups in the main chain; a slight increase in the T_g with the inclusion of an aromatic methoxy substituent; and, a dramatic decrease in the glass transition temperature upon saturation of the main chain C=C double bond to a single bond. Also, as the polymer main chain unsaturation increased, their solubility and tractability decreased, leading to a lower molecular weight analysis, which could be real or simply a result of diminished solubility.

Future work will test mechanical properties in addition to the degradation behaviour of the polymers and copolymers. The general similarity of these polymers to lignin suggests biodegradation to be likely. Degradation pathways via simple hydrolytic degradation are also conceivable and yield by-products that are not just benign, but beneficial to human health.²⁴

Acknowledgements

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References

- 1 "Global Styrene Production Exceeded 26.4 Million Tonnes in 2012," Merchant Research & Consulting, Ltd. <http://mcgroup.co.uk/news/20130830/global-styrene-production-exceeded-264-million-tonnes.html>. 19.8 million tons of PET produced were reported for 2012. In 2012, there were about 288 million tons of plastics produced globally. <http://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/>.
- 2 J. J. La Scala, C. A. Ulven, J. A. Orlicki, R. Jain, G. R. Palmese, U. K. Vaidya and J. M. Sands, *Clean Technol. Environ. Policy*, 2007, **9**, 265–279.
- 3 Environmental Protection Agency, Federal Register, 2003, **68**, 19375–19443.
- 4 U. S. Department of Health and Human Services, Public Health Services, National Toxicology Program 12th Report on Carcinogens, 2011.
- 5 S. E. Lebo Jr., J. D. Gargulak and T. J. McNally, in *Lignin Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., New York, 2001, vol. 15, pp. 1–32.
- 6 M. Sindhu and T. E. Abraham, *Crit. Rev. Biotechnol.*, 2004, **24**, 59–83.
- 7 F. Shahidi, in *Natural Antioxidants: Chemistry, Health Effects, and Applications*, AOCS Press, 1997.
- 8 C. Y. Lee, A. Sharma, R. L. Uzarski, J. E. Cheong, H. Xu, R. A. Held, S. K. Upadhyaya and J. L. Nelson, *Free Radical Biol. Med.*, 2011, **50**, 918–925.
- 9 L. R. Ferguson, S. Zhu and P. J. Harris, *Mol. Nutr. Food Res.*, 2005, **49**, 585–693.
- 10 K. Kikugawa, T. Hakamada, M. Hasunuma and T. Kurechi, *J. Agric. Food Chem.*, 1983, **31**, 780–785.
- 11 M. Kampa, V. I. Alexaki, G. Notas, A. P. Nifli, A. Nistikaki, A. Hatzoglou, E. Bakogeorgou, E. Kouimtzoglou, G. Blekas, D. Boskou, A. Gravanis and E. Castanas, *Breast Cancer Res. Treat.*, 2004, **6**, 63–74.
- 12 Y. S. Lee, *Arch. Pharmacol. Res.*, 2005, **28**, 1183–1189.
- 13 L. Mialon, A. G. Pemba and S. A. Miller, *Green Chem.*, 2010, **12**, 1704–1706.
- 14 L. F. Charbonneau and N. J. Morris, *Thermotropic polyesters derived from ferulic acid and a process for preparing the polyesters*, U.S. Pat, 4230817, 1980 (Celanese Corporation).
- 15 L. H. Sperling, *Introduction to Physical Polymer Science*, 4th edn, Wiley, Hoboken, 2006, pp. 410–412.
- 16 L. Mialon, R. Vanderhenst, A. G. Pemba and S. A. Miller, *Macromol. Rapid Commun.*, 2011, **32**, 1386–1392.
- 17 W. Dong, H. Li, M. Chen, Z. Ni, J. Zhao, H. Yang and P. Gijssman, *J. Polym. Res.*, 2011, **18**, 1239–1247.
- 18 S. Sasiwilaskorn, P. Klinubol, A. Tachaprutinun, T. Udomsup and S. P. Wanichwecharungruang, *J. Appl. Polym. Sci.*, 2008, **109**, 3502–3510.
- 19 M. Satomura, *Unsaturated polyester ether having a photocrosslinkable moiety*, US Pat, 4053415, 1977.
- 20 N. Makoto and N. Hyogo, *Method for producing phase retarder films*, E. Pat, 0883016, 1998.

- 21 O. Kreye, S. Oelmann and M. A. R. Meier, *Macromol. Chem. Phys.*, 2013, **214**, 1452–1464.
- 22 H. T. H. Nguyen, E. R. Suda, E. M. Bradic, J. A. Hvozdoch and S. A. Miller, *Polyesters from Bio-Aromatics*, ACS Symposium Series Green Polymer Chemistry III: Biobased Materials and Biocatalysis, ed. H. N. Cheng, R. Gross and P. Smith, 2015, ch. 24, vol. 1192, pp. 401–409.
- 23 T. G. Fox, *Bull. Am. Phys. Soc.*, 1956, **1**, 123–124.
- 24 G. Thuillier, Method of Preparing 3-methoxy-(β -hydroxy-ethoxy)-4-cinnamic acid, *Fr. Pat.*, 2306968, 1976.