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Terpolymers from Lactide and Bisphenol A Derivatives: Introducing Renewable Resource Monomers into Commodity Thermoplastics

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Over the past few decades, significant work has been devoted to enhancing the properties of bio-based polymers with the hope of approaching the performance of, and/or make compatible with, commodity plastics. Polylactide (PLA) derivatives are the primary focus of this effort and are today produced as the largest scale renewable resource plastic.[1] The synthesis of PLA is generally carried out by the ring-opening polymerization of lactide monomer which is obtained by the dimerization of lactic acid—a product of corn sugar fermentation. The relatively low glass transition temperature ($T_g \sim 60$ °C) of PLA and its modest impact resistance, however, limit its widespread use and thus viable competition with traditional plastics such as polystyrene and other polyolefins which dominate low-cost packaging and fiber markets.

Recent approaches to enhance the properties of lactide-derived plastics include polymerization of lactide using single site catalysts[2] as well as plasticization, blending, and copolymerization.[3] Here we report the first synthesis of terpolymers of L-lactide (LA), with commodity monomers such as 4,4′-hexafluoroisopropylidenediphenol (6F-Bis-A) and the diglycidyl ether of bisphenol A (DGEBA) using metal halide−crown ether complexes (Scheme 1). In addition, corn-derived ethyl lactate is demonstrated to be an excellent solvent for the terpolymerization and represents a promising and general approach for addressing current environmental issues. 18-Crown-6/KCl (18C6/KCl) complexes have been successfully used for the polymerization of bis(epoxide)s with acid chlorides or active di(ester)s[4] and diphenyl carbonates;[5] however, lactide polymerization or copolymerization catalyzed by metal halide−crown ether complexes was not known previously.

In this study, we systematically investigated the effect of monomer feed ratio and solvent on the terpolymerization of LA with 6F-Bis-A and DGEBA catalyzed by 18C6/KCl. The terpolymerization with 1:1:1 monomer ratio at 110 °C for 24 h produced high molecular weight ($M_n > 32\,000$) terpolymer with molecular weight distribution (M_w/M_n) near 2. Polymerizations with higher LA ratios yielded low molecular weight dark brown reaction mixtures (Table 1). Among the number of polymerization solvents evaluated, 1-phenoxy-2-propanol (Dowanol) and ethyl lactate produced the best results, giving high molecular weight film forming terpolymer (**1**, **10**) in good yield (>85%).

Scheme 1. Terpolymerization of Lactide and Bisphenol A Derivatives

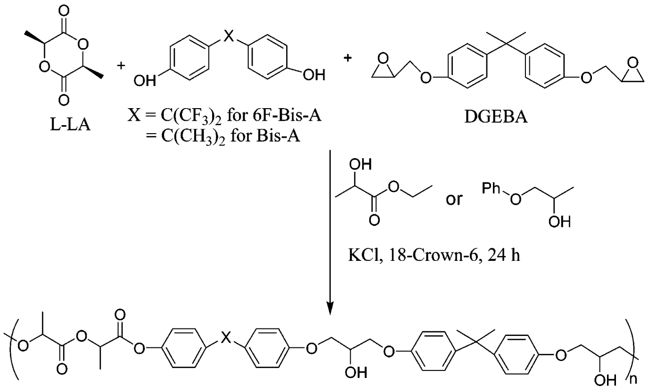

Table 1. Selected Conditions and Properties of the Polymers

polymer	LA:6F-Bis-A:DGEBA[a]	solvent	M_n [b] ($\times 10^{-3}$)	M_w/M_n [b]
1	1:1:1	Dowanol[c]	46	2.3
2	2:1:1	Dowanol	11.1	1.5
3	1:2:2	Dowanol	22	1.6
4	0:1:1	Dowanol	21	1.7
5	1:1:0	Dowanol	*d*	
6	1:0:1	Dowanol	1.24	5.2
7	1:1:1	neat	13.7	3.5
8	1:1:1	toluene	10.4	2.0
9	1:1:1	diglyme	13.5	1.8
10	1:1:1	ethyl lactate	32	1.9

[a] Monomer molar ratio with 18C6/KCl (1 mol %) in 50 wt % solvent at 110 °C for 24 h. [b] GPC in CHCl$_3$ vs polystyrene. [c] PhOCH$_2$CH(CH$_3$)OH. [d] No polymer.

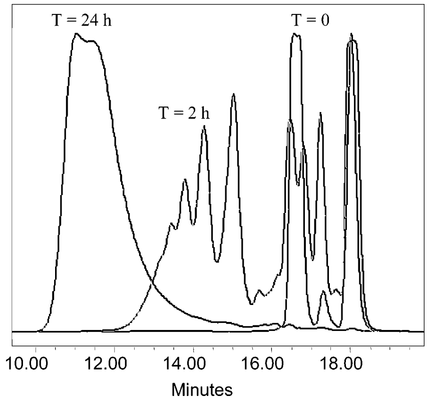

Figure 1. Evolution of molecular weight by GPC for advancing terpolymer **1** at 0, 2, and 24 h.

Figure 1 illustrates the molecular weight evolution for terpolymer **1** by gel permeation chromatograpy (GPC). Terpolymerization carried out without a catalyst produced low molecular weight (GPC, $M_n = 1800$ and $M_w/M_n = 2.2$) opaque oligomers even after 72 h. Remarkably, green solvent ethyl lactate facilitated the terpolymerization as well as Dowanol, and to our knowledge, this is the first account of its use as a LA polymerization solvent. The step-growth polyaddition of 6F-Bis-A and DGEBA without lactide under the same conditions produced copolymer **4** with reasonable molecular weight (Table 1).

Monomer conversion during terpolymerization was monitored by in situ FTIR spectroscopy (ReactIR).[7,8] The strong lactide C=O (1770 cm^{-1}) vibration shifted to 1740 cm^{-1}, and the epoxy stretch (915 cm^{-1}) of DGEBA

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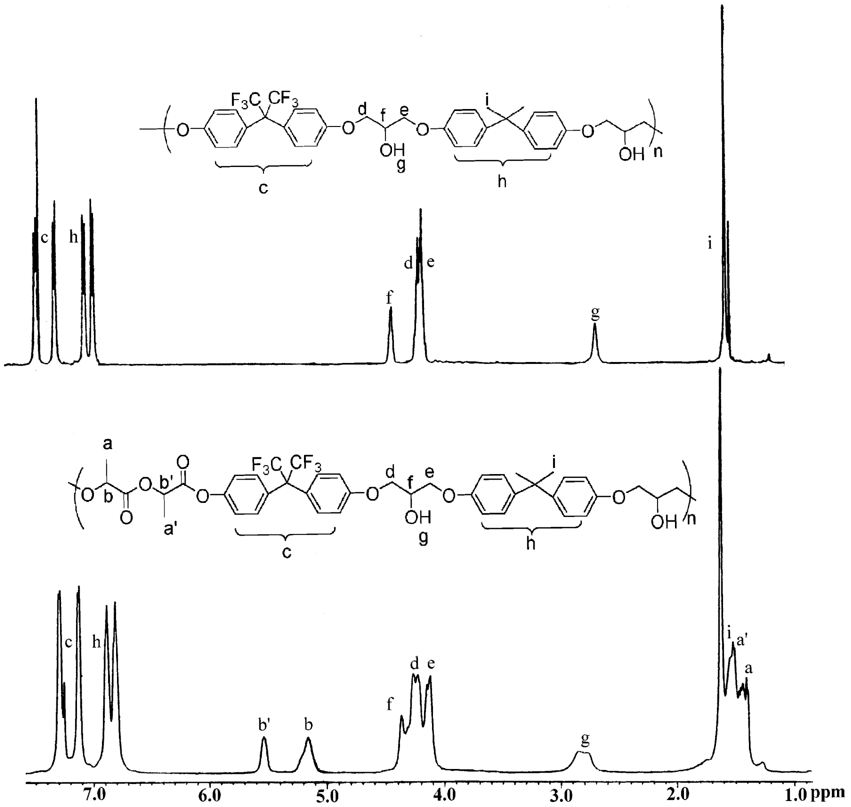

Figure 2. ^{1}H NMR spectrum of copolymer **4** (above) and terpolymer **10** (below).

disappeared upon polymerization.[7] A real time profile generated using the characteristic bands at 1770, 915, 1238 cm^{-1} (lactide $-$CO$-$O$-$), 1186 cm^{-1} (lactide$-$phenoxy $-$CO$-$OPh$-$), and 1132 cm^{-1} (lactide$-$DGEBA $-$O$-$CH$_2$CH(OH)$-$) indicated similar rates for lactide and DGEBA monomer conversion during terpolymerization.[7]

The ^{1}H NMR spectrum of terpolymer **10** illustrates the selectivity of alternating comonomer enchainment where lactide$-$lactide defects are not favored (Figure 2). Polymer **10** exhibits signals at 5.16 and 5.53 ppm (multiplet) representing the ring-opened lactide α-methine protons. The peak area integration[6] of the 5.16 ppm signal (b′, 1H), the aromatic signals (c+h, 16.2H), the hydroxyl ether proton signals (d+e+f, 9.5H), and the hydroxyl signals (g, 1.7H) are very close to the theoretical integration of 16, 10, and 2, respectively, and support the terpolymer structure shown in Scheme 1. The ^{13}C NMR spectrum as well as elemental analysis of the terpolymer further supports these results and the proposed isolated lactide linkages.[7] The minor shoulder observed in the α-methine proton signal at 5.16 ppm (b, Figure 2) is possibly due to difficult to remove byproducts, lactide$-$lactide enchainment, or end groups.

To probe the relative reactivity ratios for the monomers, a series of polymerizations were performed under identical conditions with the following combinations (i) LA and 6F-Bis-A, (ii) LA and DGEBA, (iii) LA, DGEBA, and 6F-Bis-A, and (iv) 6F-Bis-A and DGEBA and studied by ReactIR spectroscopy and GPC. Lactide and epoxide monomer conversions in each case were monitored by the decrease of either the carbonyl peak intensity at 1770 cm^{-1} or epoxide peak intensity at 915 cm^{-1}. From these data, the following order of decreasing reaction rate can be inferred: LA + DGEBA > 6F-Bis-A + DGEBA > LA + 6F-Bis-A, which supports the formation of isolated 6F-Bis-A/DGEBA adducts in the terpolymer.[7] Lactide monomer, in fact, is consumed at a faster rate during equal molar terpolymerization than is observed for any of the model reactions.

Interestingly terpolymerization with excess LA as well as copolymerization of LA with DGEBA yielded discolored polymers within a few hours presumably due to side reactions of unconsumed LA, which is known to give colored byproducts. Discoloration of the reaction mixture was not observed during 1:1:1 terpolymerization or during the terpolymerization with excess 6F-Bis-A or DGEBA, which suggests along with the FTIR data that the initial LA-DGEBA adduct reacts with 6F-Bis-A. Although the mechanism is unclear, in situ FTIR and GPC results indicate the rapid formation of a propagating species containing all three monomers (possibly an AB species terminated with glycidal ether and phenolic groups), which then proceeds in classical step-growth fashion. These results are consistent with the formation of a terpolymer with 1:1:1 insertion of each monomer as shown in Scheme 1. A detailed kinetic and mechanistic study of the terpolymerization is currently underway.

Terpolymers **1** and **10** produced colorless transparent films upon solution casting from tetrahydrofuran. The tough flexible films could be creased without cracking, and a complete mechanical and gas permeability/selectivity study will be published elsewhere. The thermal properties of the polymers were analyzed by DSC, and the amorphous terpolymers **1** and **10** exhibited a $T_g = 80$ °C whereas copolymer **4** gave a $T_g = 110$ °C. For comparison, terpolymerization with bisphenol A monomer substituting for 6F-Bis-A was also accomplished. As expected, the T_g of the latter nonfluorinated version was slightly lower (76 °C).

In summary, the terpolymerization of LA, 6F-Bis-A, and DGEBA gave novel high molecular weight poly(ester hydroxy ether)s containing isolated lactide units. This method may be applicable to the development of new commodity thermoplastics containing a significant content of renewable resource material. The potential impact of this technology to epoxy markets alone addresses directly the US Depatment of Energy's "Crop/Plant Based Renewable Resource 2020" vision.[9]

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Supporting Information Available: Experimental procedures, ReactIR data, ^{13}C NMR data, and DSC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Typical polymerization procedure for terpolymerization: To a 150 mL three-neck round-bottom flask fitted with Friedrich's condenser septum and overhead stirrer, 0.472 g (1.34 mmol) of DGEBA, 0.467 g (1.34 mmol) of 6F-Bis-A, 0.2 g (1.34 mmol) of LA, and 0.569 g (50 wt %) of ethyl lactate were added. The temperature was increased to 110 °C with stirring, and 0.035 g (0.0134 mmol) of 18C6 and 0.009 g (0.0134 mmol) of KCl were added. After stirring for 24 h, the contents were diluted with THF to 20 wt % and precipitated into vigorous stirring methanol and repeated with *n*-hexane and then dried, giving a white solid (**1** or **10**) in >85% yield. The molecular weight and molecular weight distribution of the homo- and copolymers were obtained at ambient temperature using a Waters 2690 Alliance system equipped with 2410 refractive index and 996 photodiode array detectors. FTIR (neat film) (cm^{-1}): 928, 951, 967, 1042, 1132, 1173, 1206, 1250, 1297, 1502, 1586, 1600, 1744, 2875, 2930, 2963, 3425. ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.39−1.8 (15H, m, CH$_3$), 2.8 (1.7H, m, OH), 4.1−4.4 (9.5H, m), 5.16 (1.5H, m, α-H LA), 5.53 (1H, m, α-H LA), 6.72−7.0 (8.1H, m, aromatic), 7.0−7.4 (8.1H, m, aromatic). ^{13}C NMR (125 MHz, CDCl$_3$) δ: 16.6, 21.0, 30.9, 42.0, 68.7, 69.0, 113.9, 126.0, 127.7, 131.6, 143.5, 156.2, 158.6, 169.0, 176.0. ^{19}F NMR (470 MHz, CDCl$_3$) δ: −64.00. Anal. Calcd (Found): C, 61.45 (61.95); H, 5.15 (5.20); O, 19.49 (17.68); F, 13.88 (14.25)%.

(7) See Supporting Information.

(8) See, for example: (a) Aubrecht, K. B.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **2002**, *35*, 644. (b) Pasquale, A. J.; Allen, R. D.; Long, T. E. *Macromolecules* **2001**, *34*, 8064.

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