

Perfectly Alternating Copolymer of Lactic Acid and Ethylene Oxide as a Plasticizing Agent for Polylactide

Kevin Bechtold, Marc A. Hillmyer,* and William B. Tolman*

Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455-0431

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ABSTRACT: The ring-opening polymerization of 3-methyl-1,4-dioxan-2-one (MDO) mediated by a catalytic system composed of $Y[N(TMS)_2]_3$ and benzyl alcohol (BnOH) led to a new polymer (PMDO) comprised of perfectly alternating lactic acid and ethylene oxide repeat units. Samples of PMDO were characterized by NMR spectroscopy, size exclusion chromatography (SEC), and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). In a series of MDO polymerizations ($[MDO]_0 = 3.0$ M in toluene, between -30 and 60 °C), the equilibrium monomer concentrations were measured. The thermodynamic parameters for the polymerization reaction were determined: $\Delta H_p^\circ = -12.1 \pm 0.5$ kJ mol $^{-1}$ and $\Delta S_p^\circ = -42 \pm 2$ J mol $^{-1}$ K $^{-1}$. The glass transition temperature (T_g) of PMDO was determined to be ≈ -24 °C by differential scanning calorimetry and found to vary little over the molecular weight range studied (3–21 kg/mol). Mixtures of low-molecular-weight PMDO and atactic polylactide (PLA) were prepared by solution casting and subsequent annealing significantly above the T_g 's of the individual components. Miscibility of PLA and PMDO was evinced by single T_g 's that were well-described by the Fox relationship for miscible blends. Because of its miscibility with PLA and low T_g , PMDO has potential as a macromolecular plasticizing agent for commercially relevant PLA.

Introduction

Biodegradable and biorenewable polymers that do not rely on petrochemical-based feedstocks and decompose into nontoxic byproducts are environmentally friendly alternatives to current commodity polymers.¹ One such material, polylactide (PLA, Scheme 1), is particularly significant since it is derived from fermentation of corn starch and other abundant naturally occurring biomass² and ultimately may be degraded to carbon dioxide and water.³ PLA and its copolymers are currently used in biomedical applications,^{4–6} but a broad substitution of PLA for traditional plastics will require increased diversification beyond the parent polymer.^{7,8}

The tensile properties of PLA are generally characterized by a rather low elongation at break and moderate impact resistance.² These features can restrict the use of the unmodified polymer for flexible blown and cast film applications.³ Lowering the T_g of amorphous PLA (≈ 60 °C), which lies above typical use temperatures, is a strategy used to toughen the parent polymer. Methods to lower the T_g of PLA have generally involved synthesis of copolymers^{9–14} or physical blending with plasticizing agents^{15–20} (often an economical alternative to copolymerization schemes). While low-molecular-weight substances are typically the best plasticizing agents,²¹ in applications such as food packaging, low-molecular-weight materials are often not appropriate because of problems with leaching.^{15,22} Polymeric plasticizing agents can attenuate the leaching problem, but two-component systems containing high-molecular-weight materials generally exhibit unfavorable thermodynamics of mixing, leading to macrophase separation, poor interfacial adhesion, and inferior mechanical properties.²³ The ideal plasticizing agent for PLA packaging materials would be miscible with PLA, significantly lower the T_g ,

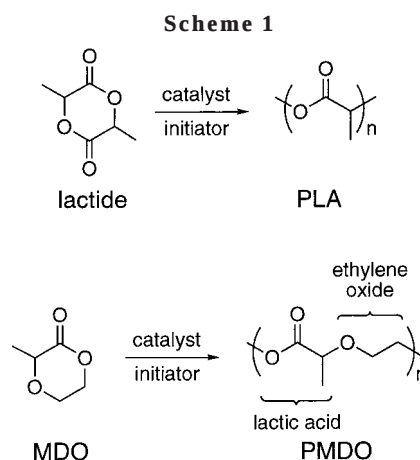


exhibit biodegradable characteristics, and would be minimally leached.

Poly- ϵ -caprolactone,²⁰ poly(3-hydroxy butyrate),¹⁸ thermoplastic starch,¹⁷ oligomeric PLA,⁸ and poly(ethylene oxide) (PEO)²⁴ have all been investigated as potential plasticizing agents for PLA. Of the miscible materials, PEO exhibits exceptional promise as a plasticizer due to excellent miscibility with PLA (even at high molecular weights²⁴) and drastic improvement in elongation at break and impact resistance at low PEO loadings.¹⁶ However, in one reported example, high PEO loadings (above 50%) in PLA led to some macrophase separation due to crystallization of the PEO.²⁵ Furthermore, because of the hydrophilic nature of PEO, even mild aqueous extraction can result in extensive leaching of PEO from the host polymer.²⁶ The crystallinity and hydrophilicity of PEO are drawbacks to this otherwise useful plasticizer.

To combat some of PEO's deficiencies, block copolymers of PLA and PEO have been synthesized and investigated as PLA plasticizers.²⁷ The plasticization

* To whom correspondence should be addressed. E-mail: hillmyer@chem.umn.edu; tolman@chem.umn.edu.

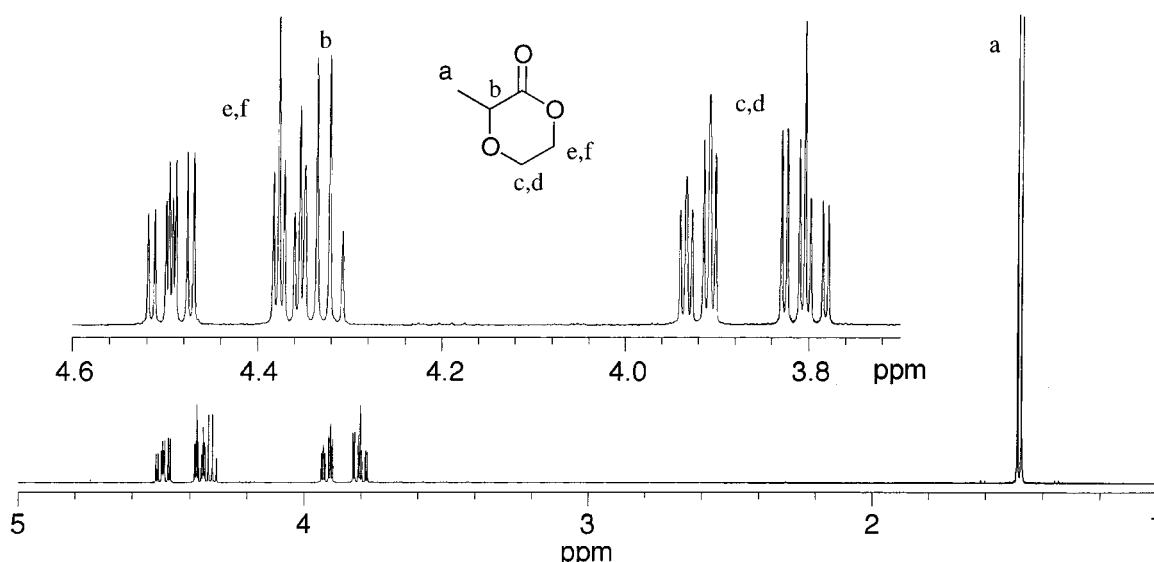


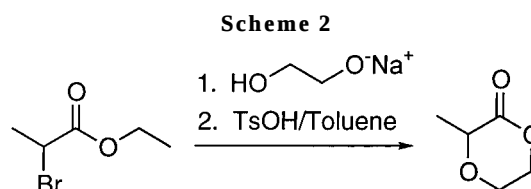
Figure 1. ^1H NMR spectrum of MDO (500 MHz, CDCl_3).

behavior for these compounds is complicated due to a dependence on the PEO block length; some samples exhibited microphase separation and crystallization of the PEO blocks, resulting in incomplete plasticization of the host polymer. In a separate strategy, the direct copolymerization of L-lactide with ethylene oxide was reported to yield copolymers having a multiblock structure.²⁸ Films formed from blends of these copolymers and PLA exhibited improved film moduli and yield strengths as well as comparable elongations at break relative to PLA/PEO homopolymer blends of identical composition. Leaching of these copolymer plasticizing agents was proposed to be greatly reduced compared to the case of PEO. Although some control over the individual block sizes was exerted through variation of the reaction conditions, all of the reported samples exhibited two melting transitions, indicating that the blocks were of sufficient length to undergo crystallization-induced microphase separation.

On the basis of the aforementioned considerations, we hypothesized that a polymer comprised of perfectly alternating lactic acid and ethylene oxide units would be an efficient PLA plasticization agent. To test this notion, we developed a preparative route to this polymer by the ring-opening polymerization of 3-methyl-1,4-dioxan-2-one (MDO, Scheme 1). The polymerization thermodynamics were examined, and the new polymer (PMDO) was characterized. Finally, the potential utility of PMDO as a macromolecular plasticizing agent for PLA was revealed through examination of the thermal behavior of PMDO and PMDO/PLA blends.

Results and Analysis

Monomer and Polymer Synthesis. The preparation of MDO was based on a previous method⁴⁴ reported for the synthesis of analogues in which the methyl group is replaced by longer alkyl chains (Scheme 2). In a key difference from the reported sequence, we found that the initial reaction of the monosodium salt of ethylene glycol with racemic ethyl-2-bromopropionate did not provide the intermediate ethyl-2-(2-hydroxyethoxy)-propionate cleanly and instead yielded a mixture of compounds, including some MDO (GC/MS). After several failed attempts at purifying the intermediate, the



mixture was treated directly with *p*-toluenesulfonic acid to complete the intramolecular transesterification. Pure racemic MDO was then isolated after chromatographic purification in an overall yield of $\approx 20\%$. The identification of MDO was accomplished by ^1H and ^{13}C NMR and FTIR spectroscopy as well as high-resolution mass spectrometry. Of particular note is the ^1H NMR spectrum (Figure 1), which exhibits complex, yet well-resolved, splitting patterns for the diastereotopic ring protons (inset) in the chiral molecule.

For the polymerization of MDO we chose to use a yttrium alkoxide initiator.^{29–33} An easily prepared system with previously demonstrated high reactivity²⁹ may be prepared “in situ” by the reaction of $\text{Y}[\text{N}(\text{TMS})_2]_3$ with alcohols. We successfully polymerized MDO by adding a solution of $\text{Y}[\text{N}(\text{TMS})_2]_3$ in toluene to a solution of BnOH and excess MDO in toluene with rapid stirring at ambient temperature (Scheme 1; see Experimental Section for details). Conversion of MDO was determined using ^1H NMR spectroscopy (Figure S1). Quenching of the polymerization was accomplished in most cases by exposure to air, followed by dissolution in a minimum amount of CHCl_3 and precipitation from excess cold pentane.³⁴ Polymerizations were quite rapid; for the reaction of MDO (100 mg, 8.6×10^{-4} mol) with BnOH (10 μL of 1.0 M toluene solution, 1×10^{-5} mol) and $\text{Y}[\text{N}(\text{TMS})_2]_3$ (20 μL of 0.05 M toluene solution, 1×10^{-6} mol) conversions of 75, 78, and 80% were determined for samples taken at 0.5, 2, and 24 h, respectively. In this example, the viscosity of the solution increased so rapidly that stirring ceased less than 30 s after the catalyst was added.

The product polymer was characterized by NMR spectroscopy, size exclusion chromatography (SEC), and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). Shown in Figure 2 is the MALDI-MS spectrum for a low-molecular-weight PMDO sample.

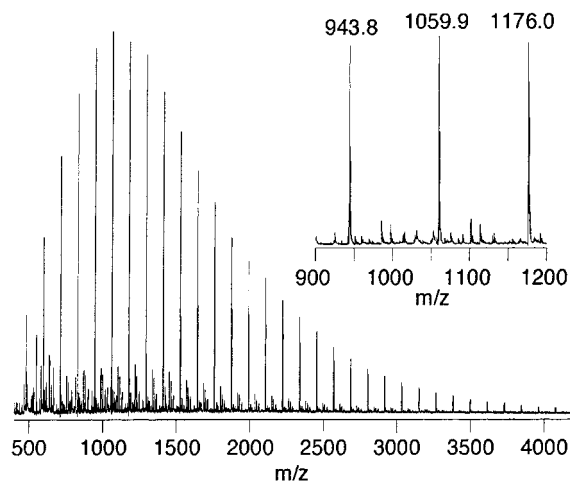


Figure 2. MALDI-MS of BnOH-terminated PMDO synthesized in the bulk using a MDO/BnOH/Y[N(TMS)₂]₃ ratio of 100/10/1. The masses of the labeled peaks correspond to the sum of an integer number of monomer units, one benzyl alcohol unit (end group), and a sodium ion from the matrix.

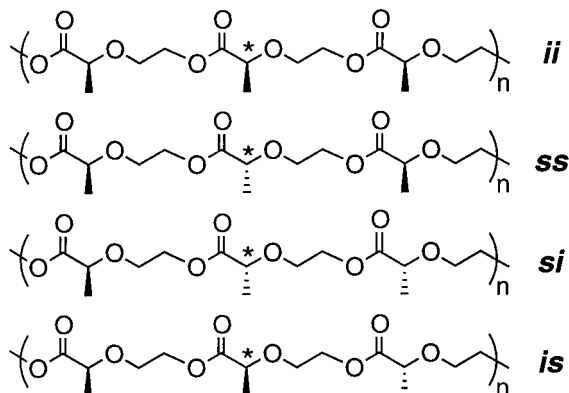
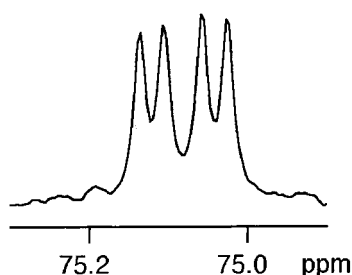


Figure 3. Portion of the ¹³C{¹H} NMR spectrum (125 MHz, CDCl₃) of atactic PMDO showing methine carbon (*) signals and the relevant polymer stereosequences at the triad level (i = isotactic pair, s = syndiotactic pair).

The data indicate the presence of predominantly benzylalkoxy/hydroxyl-terminated polymers with a repeat unit mass identical to that of the monomer used (116.1 Da), confirming that the sample is in fact comprised of ring-opened MDO.³⁵ The presence of the hydroxyl end group indicates that the reaction is quenched when the propagating end group (presumably a L_nY-OR species) is protonated, possibly as a result of water vapor admitted to the reaction upon exposure to air. The NMR data of the polymer are consistent with an atactic material, the observation of four peaks of equal intensity for the methine carbon in the ¹³C{¹H} NMR spectrum being particularly telling (Figure 3). Analysis of the polymer stereochemistry at the triad level predicts chemical shift inequivalence for the central methine

Table 1. Data for the Room Temperature Polymerization of MDO^a

entry	$M_0/I_0/C_0$ ^b	$M_N(\text{theor})^c$	$M_N(\text{NMR})^d$	M_N ^e	M_W ^e	PDI ^e
1	260/6.4/1	3.5	3.0	3.4	7.2	2.08
2	260/3.2/1	7.0	6.5	5.4	12.6	2.36
3	260/1.6/1	14.0	10.0	6.7	18.6	2.80
4	260/0.8/1	27.9	16.4	6.3	22.2	3.52
5	260/0.4/1	55.8	20.8	6.6	31.8	4.80

^a All samples at 74% conversion after 18 h; molecular weights are given in kg mol⁻¹. ^b Initial MDO/BnOH/Y[N(TMS)₂]₃ mole ratio. ^c At 74% conversion. ^d ¹H NMR integration of benzyl ester end group to polymer, assuming one chain per end group, and no other polymeric species present. ^e Determined by SEC (see Experimental Section).

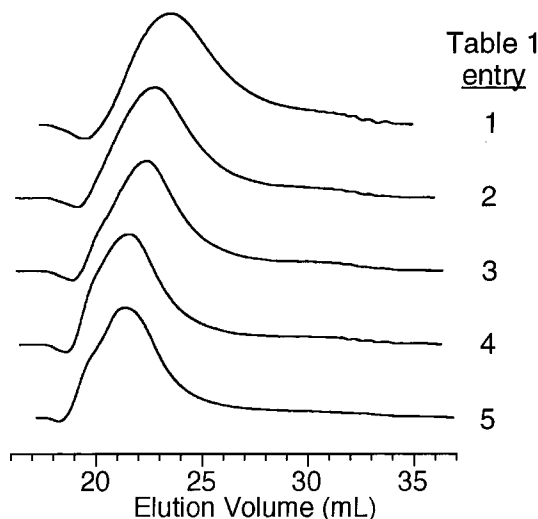


Figure 4. SEC traces of the polymers listed according to their entries in Table 1.

carbon in each of the four possible triads. The relative integration ratio for these four resonances is 1:1:1:1, as expected for an atactic polymer.³⁶

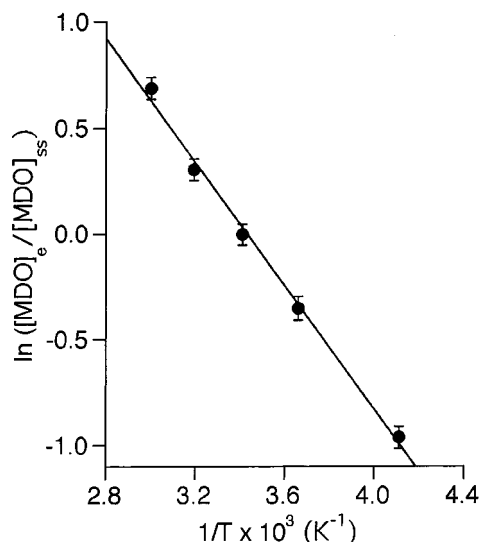
In polymerizations with various amounts of BnOH, ¹H NMR spectroscopy revealed that all of the BnOH was incorporated as benzyl ester end groups (cf. Figure S1) regardless of the [BnOH]₀/[Y[N(TMS)₂]₃]₀ ratio, indicating that BnOH is an effective chain transfer agent in this system. The PMDO samples had M_N values (by ¹H NMR spectroscopy) that were inversely proportional to the concentration of BnOH used in the polymerization, as expected, although the agreement between the theoretical and measured molecular weights was marginal at low BnOH loadings (Table 1). This discrepancy may be due to the low-level presence of hydroxyl-containing impurities in the MDO feed that act as fortuitous initiators. By SEC these polymers exhibited tailing toward lower molecular weights, leading to broad polydispersities (Figure 4). The reason for this tailing is unclear; it may be a result of mass-transfer limitations in these extremely rapid polymerizations. In all cases, the yield of PMDO was about 74%. This corresponds to an equilibrium monomer concentration of 1.6 M under these conditions ([MDO]₀ ≈ 6 M, T ≈ 35 °C in an inert atmosphere glovebox).

Polymerization Thermodynamics. Polymerizations of MDO were performed over a range of temperatures, and the equilibrium monomer concentrations ([M]_e) were determined. Because of the high viscosity observed in bulk polymerization of MDO, solution polymerization in toluene was used for these experiments; using [MDO]₀ = 3.0 M allowed for a suitable

Table 2. Equilibrium Monomer Concentrations as a Function of Temperature for the Polymerization of MDO

temp (°C) ^a	conv (%) ^b	[MDO] _e ^b	temp (°C) ^a	conv (%) ^b	[MDO] _e ^b
-30	88	0.38	40	55	1.4
0	77	0.70	60	34	2.0
20	67	1.0			

^a Uncertainty is ± 0.5 °C. ^b These values were determined by ¹H NMR integration, and the uncertainties are estimated to be $\sim 5\%$.

**Figure 5.** Plot of $\ln([MDO]_e/[MDO]_{ss})$ vs $1/T$ with a linear fit to eq 1.

range of conversions to be observed. Polymerizations were performed over the temperature range of -30 to 60 °C. The reactions were monitored by in situ FTIR spectroscopy (ReactIR), with the equilibrium conversion being indicated when the absorptions of two monomer bands (2984 and 2877 cm^{-1}) remained constant. Although in most cases equilibrium was attained in less than 1 h, the reactions were not exposed to air until at least 1 h after equilibrium was initially indicated, at which point a sample was withdrawn for ¹H NMR spectroscopic analysis to determine the extent of polymerization. Measured conversions and equilibrium monomer concentrations $[MDO]_e$ as a function of temperature are listed in Table 2.

The concentration of monomer at equilibrium exhibits a temperature dependence according to the equation³⁷

$$\ln\left(\frac{[M]_e}{[M]_{ss}}\right) = \frac{\Delta H_p^0}{RT} - \frac{\Delta S_p^0}{R} \quad (1)$$

where ΔH_p^0 is the standard state enthalpy of polymerization and ΔS_p^0 is the standard state entropy of polymerization ($[MDO]_{ss} = 1$ M). A plot of $\ln([MDO]_e/[MDO]_{ss})$ vs $1/T$ (Figure 5) was fit to a line and yielded $\Delta H_p^0 = -12.1 \pm 5$ kJ mol^{-1} and $\Delta S_p^0 = -42 \pm 2$ $\text{J mol}^{-1} \text{K}^{-1}$.

Thermal Behavior of PMDO and PMDO/PLA Blends. The T_g values for the PMDO samples were determined by DSC. For the majority of PMDO samples we prepared the T_g values were between -19 and -26 °C.³⁸ No correlation was observed between the T_g values and the molecular weights of the PMDO samples. In one experiment a sample of PMDO was heated from -30

Table 3. Glass Transition Temperatures (T_g) for PMDO/PLA Blends As Measured by DSC

PLA weight fraction ^a	T_g (°C)	transition breadth (°C) ^b	PLA weight fraction ^a	T_g (°C)	transition breadth (°C) ^b
0	-21	10	0.53	4	24
0.16	-16	8	0.75	27	19
0.35	-5	20	1	53	10

^a Weight fraction = mass PLA/(mass PMDO + mass PLA). Estimated uncertainty in these values is ± 0.05 . ^b Estimated temperature difference determined from the crossing points of the transitional heat flow curve with the tangent lines fit to the heat flow curve before and after the transition.

to 180 °C, and only a T_g at -19 °C was observed. There was no evidence of melting or crystallization of the PMDO over this temperature range.

To investigate the use of PMDO as a plasticizing agent for PLA, blends of the polymers were obtained by solution casting from CDCl_3 . Samples of relatively high-molecular-weight PLA ($M_N = 38.3$ kg mol^{-1} , $\text{PDI} = 1.64$) were blended with low-molecular-weight PMDO ($M_N = 4.6$ kg mol^{-1} , $\text{PDI} = 2.55$) in different ratios. To remove solvent and any other small molecule impurities that might contribute to the plasticization, samples were annealed at 90 °C for 2 h in vacuo. Characterization of the blends by ¹H NMR spectroscopy both before and after annealing showed that the compositions remained constant to within 2% for every sample. Furthermore, transesterification of the PMDO and PLA was minimal under these annealing conditions, as indicated by GPC traces of the blends that were superpositions of traces for the starting polymers. All of the blends were optically clear materials with physical consistencies that ranged from a hard solid for pure PLA to a viscous liquid for pure PMDO.

DSC was used in order to determine the T_g values for the blends of varying weight fraction compositions. All samples were subjected to identical thermal histories before analysis (see the Experimental Section). A single glass transition temperature was observed for each sample (Table 3, Figure S2). In most cases, the transition breadth of the blends is larger than that of the constituents. The dependence of T_g on the composition of homogeneous, miscible blends is described by eq 2, where w_i is the weight fraction of component i , T_i is the glass transition temperature of component i , and T_g is the glass transition temperature of the blend.³⁹ We found that a plot of $1/T_g$ vs the PLA weight fraction shows a linear correlation as predicted (Figure 6).

$$\frac{1}{T_g} = \frac{w_1}{T_1} + \frac{w_2}{T_2} \quad (2)$$

Discussion

The ring-opening polymerization of moderate to large rings allows for the synthesis of polymers that are chemically identical to structures that can only be obtained by a highly selective copolymerization of two or more monomers. Examples of this "ring-opening strategy" have been reported using metathesis polymerization (ROMP)⁴⁰ of cyclic olefins and metal-catalyzed polymerization of cyclic esters.⁴¹ In both of these cases the ring-opening process leads to regular alternating "copolymers" that are difficult to prepare otherwise. Anticipating that it would be overly difficult to synthesize the title polymer by a method involving alternating incorporation of its separate components

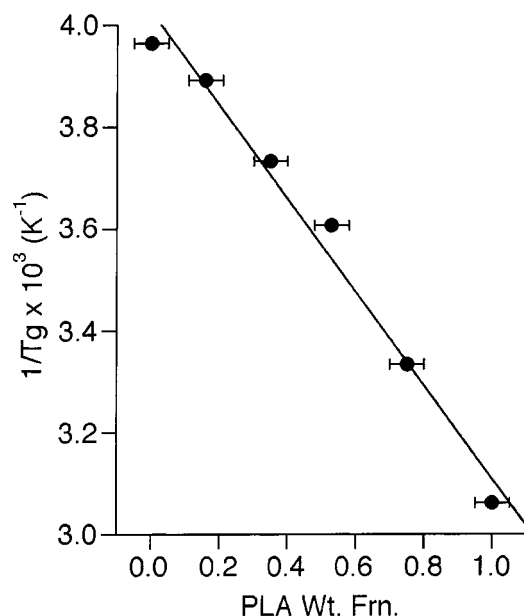


Figure 6. Plot of $1/T_g$ vs weight fraction PLA showing correspondence to eq 2.

lactic acid and ethylene oxide, we employed a “ring-opening strategy” for the preparation of a heretofore-inaccessible polymer structure, the perfectly alternating copolymer of lactic acid and ethylene oxide (Scheme 1). This macromolecule was targeted for its predicted ability to act as a polymeric plasticizer for polylactide as described in the Introduction.

While the target monomer for this system (MDO) has a relatively simple structure, the synthesis was lower yielding than anticipated. The synthesis of MDO,^{42,43} as well as those of several other 3-alkyl-1,4-dioxan-2-ones, can be found in the literature,^{44–47} but most predate modern characterization techniques. Using a protocol first reported in 1962, we were able to isolate MDO in a 20% yield, and we completely characterized it using contemporary analytical methods. Despite the low yield, the straightforward protocol using inexpensive starting materials made this an acceptable route for obtaining highly pure samples of racemic MDO in gram quantities sufficient for the subsequent polymerization studies. Because of its racemic nature, we anticipated that its derived polymer PMDO would be atactic and that, like atactic PLA, it would not crystallize. Thus, crystallization-induced phase separation would likely be avoided in the targeted PMDO/PLA blends.

We also anticipated that the ring strain in MDO that would provide the principal thermodynamic driving force for polymerization (a reversible, equilibrium process) would be considerably less than in lactide due to removal of a carbonyl group (thus changing an ester linkage to an ether). The driving force also would probably be less than in the parent 1,4-dioxan-2-one,⁴⁸ because ring alkyl substituents generally lead to a preference for the ring structure rather than the open-chain form.⁴⁹ For almost every monomer capable of being polymerized, at a given temperature there is a critical monomer concentration ($[M]_c$) below which polymerization is thermodynamically impossible. In the typical exothermic polymerization two experimental variables can be changed to affect the monomer/polymer equilibrium. At fixed temperature, increasing the monomer concentration beyond $[M]_c$ will lead to a greater

Table 4. Measured Thermodynamic Parameters for Polymerizations of Related Cyclic Esters^a

monomer	ΔH_p^0 (kJ mol ⁻¹)	ΔS_p^0 (J mol ⁻¹ K ⁻¹)	ref
MDO	-12.1	-41.6	this work
1,4-dioxan-2-one	-14.1	-45.3	48
DL-lactide	-23.9	-43.8	51, 52
ϵ -caprolactone	-28.8	-54	53

^a Values based on 1.0 M standard state concentrations of monomer and polymer repeat units.

preference for polymer. At a fixed monomer concentration, lowering the temperature will have the same effect (i.e., increased polymer concentration). Of course, to be useful the polymerization process must be kinetically feasible under the reaction conditions. As a reference for the polymerization of MDO, the $[M]_c$ at 100 °C for the parent 1,4-dioxan-2-one is 2.5 M.⁴⁸ We expected the $[M]_c$ for MDO to be higher since the driving force for polymerization (i.e., ring strain) would be lower.

With these considerations in mind, we sought to provide optimal conditions for obtaining high conversions of MDO by using a catalyst that would be sufficiently reactive to polymerize it rapidly at low temperature and by performing polymerizations at a high monomer concentration. Given the plethora of metal alkoxides capable of polymerizing cyclic esters,⁵⁰ we chose a catalyst system comprised of a yttrium(III) precursor ($Y[N(TMS)_2]_3$) and an active hydroxyl compound (BnOH). The yttrium alkoxides formed in situ in this manner had been shown previously to be extremely active cyclic ester polymerization catalysts at room temperature.²⁹

Using the aforementioned yttrium system as catalyst at room temperature with essentially neat MDO, polymerization to give PMDO proceeded smoothly to about 74% conversion. Identification of the new polymer was accomplished on the basis of NMR, MALDI-MS, and SEC data. Since BnOH has been determined to be an effective chain transfer agent for this type of yttrium-catalyzed polymerization, we explored molecular weight control of PMDO using varying amounts of BnOH. These experiments proved to be successful (Table 1), and PMDO samples with tunable molecular weights thus were realizable, a feature important for future control of PMDO properties relevant to its plasticization effectiveness.

Using initial MDO concentrations of 3 M in toluene, we measured $[M]_c$ for the polymerization over a 90 °C temperature range (Table 2), from which we determined the thermodynamic parameters for the solution polymerization. As expected, the polymerization of MDO is characterized by a typical entropy of polymerization for this type of monomer (-42 J mol⁻¹ K⁻¹) and a modest enthalpy of polymerization (-12 kJ mol⁻¹). Comparison of these values, in particular ΔH_p^0 , to those of several structurally related monomers (Table 4)^{48,51–53} confirms our prediction of a less favorable equilibrium constant for polymerization of MDO. The negative value of ΔH_p^0 for the polymerization of MDO indicates that there is a “ceiling temperature” (T_c) at which $[MDO]_e = [MDO]_0$ and above which polymerization will not take place (at $T > T_c$, $[MDO]_e > [MDO]_0$). For $[MDO]_0 = 3$ M, we calculate a T_c of 101 °C. At the lowest polymerization temperature attempted (-30 °C) using $[MDO]_0 = 3$ M, we were able to achieve almost 90% yield of PMDO ($[MDO]_e = 0.38$ M). Although experimental limitations

prevented polymerizations below $-30\text{ }^{\circ}\text{C}$, on the basis of the preliminary polymerization kinetics at this temperature (equilibrium was reached within 1 h), we believe that the yttrium system used in this work would be reasonably active at even lower temperatures.

Having successfully synthesized MDO and developed a method for its polymerization, we were able to access sufficient quantities of low-molecular-weight PMDO for PLA blending studies. A high-molecular-weight perfectly alternating copolymer of ethylene oxide and polylactic acid should show a T_g around $0\text{ }^{\circ}\text{C}$ based on the T_g 's of the parent polymers, their weight fractions in the copolymer, and the relationship shown in eq 2 (also applicable to specific copolymers). We measured the T_g of the PMDO samples to be around $-24\text{ }^{\circ}\text{C}$. Although we do not completely understand the nature of the difference, a similar discrepancy in calculated and measured T_g values has been observed for perfectly alternating copolymers of ethylene and vinyl acetate when compared with their statistical analogues.⁵⁴ All of the PLA/PMDO blends exhibited single T_g values by DSC, consistent with miscibility of the two polymers. The DSC traces for the blends are generally broader than the respective homopolymers. Additionally, the transition breadth for the PLA-rich blends are somewhat broader than for the PMDO-rich blends. This behavior has been observed in other miscible blends, and a recent theory accounts for both the broad transitions and the asymmetry in the transition breadths based on a "self-concentration" argument.⁵⁵ Finally, the T_g values could be reasonably fit to the Fox equation³⁹ (eq 2) for miscible blends that is based on the T_g values of the homopolymers and the composition of the blends (Figure 6).

Conclusion

In this work we have demonstrated the applicability of a method for producing the perfectly alternating copolymer of lactic acid and ethylene oxide from the ring opening of the appropriate cyclic ester monomer. Starting from inexpensive starting materials, the monomer, MDO, was successfully synthesized in sufficient yield for polymerization and miscibility studies. Using a highly active "in situ" formed catalyst, MDO was successfully polymerized to yield PMDO of varying molecular weights, which could be partially controlled by the stoichiometry of the reaction. Exploiting the high activity of the catalyst, successful solution polymerizations were carried out at very low temperatures ($-30\text{ }^{\circ}\text{C}$) and over a large temperature range (-30 to $60\text{ }^{\circ}\text{C}$). Determination of the equilibrium monomer concentrations for these polymerizations allowed the calculation of the thermodynamic parameters of polymerization. The low-temperature polymerization technique successfully employed in this work can potentially be extended to gain practical access to novel polymers obtained from cyclic esters having low enthalpies of polymerization. Blends of atactic PLA with PMDO were successfully prepared by casting from solution. DSC studies revealed that the blends were completely miscible at all compositions, as evidenced by single glass transitions. This result confirmed our hypothesis that, by incorporating lactic acid "comonomer" units with ethylene oxide units (previously shown to be effective for plasticization of PLA) in a macromolecular structure, we would be able to obtain the desired miscibility with PLA along with good plasticization behavior. Further practical applications

await more detailed examination of the physical properties of PMDO and PMDO/PLA blends.

Experimental Section

Materials. Moisture-sensitive compounds were handled in an M. Braun glovebox or by using standard Schlenk and vacuum line procedures. Toluene (Pharmco) was dried by refluxing over sodium and distilling under a nitrogen atmosphere. 1,4-Dioxane (Mallinckrodt) was dried by refluxing over sodium/benzophenone ketyl and distilling in vacuo. Benzyl alcohol was distilled from CaO. Sodium hydride (60% dispersion in mineral oil, Aldrich) was washed with pentane and dried in vacuo. Ethylene glycol (Fisher) was dried by stirring over MgSO_4 for 24 h, treating with sodium and refluxing for 4 h, and distilling in vacuo. Ethyl-2-bromopropionate (Aldrich), $\text{Y}[\text{N}(\text{TMS})_2]_3$ (Strem), and *p*-toluenesulfonic acid monohydrate (Aldrich) were used as received. Silica used for column chromatography was purchased from ICN Silitech (60 Å).

General Procedures. NMR spectra were recorded using a Varian VXR-500, VXR-300, or VI-300 spectrometer in CDCl_3 unless otherwise noted. Molecular weights (M_n and M_w) and polydispersity indices (M_w/M_n) were determined by size exclusion chromatography (SEC) using polystyrene standards. Samples were analyzed at $40\text{ }^{\circ}\text{C}$ using a Hewlett-Packard high-pressure liquid chromatograph equipped with three Jordi poly(divinylbenzene) columns of 10^4 , 10^3 , and 500 Å pore sizes and a HP1047A differential refractometer. Chloroform was employed as the mobile phase at a flow rate of 1.0 mL/min . The progress of selected polymerizations was observed using a Mettler Toledo ReactIR 4000 equipped with a diamond probe. Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) was performed on a Bruker Reflex III MALDI-TOF mass spectrometer. Samples were deposited in a DHB/NaI matrix, and positive ions within a mass range of $200\text{--}8000\text{ m/z}$ were detected. Internal calibration of the instrument was performed using oligonucleotide standards. High-resolution mass spectrometry using chemical ionization (HRMS-CI) was performed on a Finnigan MAT 95. The gas used was $4\%\text{ NH}_3$ in CH_4 , and a mass range of $60\text{--}650\text{ m/z}$ was scanned. GC/MS was performed on a Hewlett-Packard HP G1800A GCD system. A Nicolet Avatar 320 FT-IR system was used to obtain the IR spectrum of 3-methyl-1,4-dioxan-2-one. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter. An indium standard was used for calibration, and nitrogen was used as the purge gas. Samples with a weight range of $4.0\text{--}6.0\text{ mg}$ were loaded into aluminum pans, the mass was recorded, and the pans were sealed prior to measurement.

Synthesis of MDO. A Schlenk flask was charged with sodium hydride (3.83 g, 0.160 mol) and fitted with a condenser. 1,4-Dioxane (125 mL) was added by syringe, followed by addition of ethylene glycol (15.3 mL, 0.273 mol). The reaction was stirred and heated to $60\text{ }^{\circ}\text{C}$ under an inert atmosphere until H_2 evolution had ceased, and a uniform white suspension was obtained (ca. 4 h). A solution of ethyl-2-bromopropionate (20.0 mL, 0.154 mol) in 1,4-dioxane (50 mL) was added by syringe, and the reaction was maintained at $60\text{ }^{\circ}\text{C}$ and monitored by GC/MS until no further reaction of ethyl-2-bromopropionate was observed (ca. 1 h). The solution was filtered, and the solvent was removed in vacuo leaving a yellow oil. Toluene (300 mL) was added, followed by *p*-toluenesulfonic acid monohydrate (4.34 g, 0.0228 mol). A Dean-Stark condenser was fitted to the flask, and the solution was stirred and heated until collection of a toluene insoluble phase was no longer observed (ca. 1 h). When the reaction had cooled to room temperature, the solution was filtered and the solvent was removed in vacuo. Purification of the product was accomplished by passage through a plug of silica (hexanes/ethyl acetate, 1/1) followed by column chromatography (4:1 hexanes/ethyl acetate). The product (3.36 g, 18.8%) was obtained as a light yellow liquid that was stored frozen at $-30\text{ }^{\circ}\text{C}$ in a glovebox until use. ^1H NMR (500 MHz, CDCl_3): δ 1.48 (d, 3H, $J = 7.0\text{ Hz}$), 3.80 (ddd, 1H, $J = 12.7, 9.7, 3.0\text{ Hz}$), 3.92 (ddd, 1H, $J = 12.7, 6.4, 3.3\text{ Hz}$), 4.33 (q, 1H, $J = 6.9\text{ Hz}$), 4.37 (ddd,

^1H , $J = 11.4, 5.9, 3.0$ Hz), 4.49 (ddd, ^1H , $J = 11.4, 9.8, 3.5$ Hz) ppm. ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 169.8, 73.2, 69.1, 62.4, 18.0 ppm. FTIR (NaCl plates, thin film): ν 2987, 2873, 1743, 1277, 1220, 1136 cm^{-1} . GC-MS (EI) m/z (% relative intensity, ion): 116 (23, M^+), 73 (100). HRMS-Cl (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_5\text{H}_9\text{O}_3$, 117.0552; found, 117.0563; $[\text{M} + \text{NH}_4]^+$ calcd for $\text{C}_5\text{H}_{12}\text{NO}_3$, 134.0817; found, 134.0816.

Polymerization of MDO. Polymerizations were performed at room temperature in the glovebox. The glassware used was oven dried, treated with a solution of Me_2SiCl_2 (1.0 M in CH_2Cl_2), and oven dried at 130 °C for a minimum of 3 h before use. A vial was charged with MDO and a small amount of a solution of BnOH (0–32 μL); the amount was varied depending on the desired molecular weight of the resulting polymer. For purposes of comparison of data among different samples, toluene was then added such that the total volume of toluene and BnOH solution was 32 μL . This was followed by addition of a small amount of a solution of $\text{Y}[\text{N}(\text{TMS})_2]_3$ with rapid stirring for 18 h. Polymerizations were quenched outside the glovebox by dissolution of the polymer in a minimum amount of chloroform and precipitation from excess cold pentane. Residual monomer and solvent were removed by heating in vacuo for 2 h at 80 °C. An example of a typical polymerization is given as follows. A vial was charged with MDO (0.150 g, 0.001 29 mol), a solution of BnOH (16 μL , 1.0 M in toluene), and toluene (16 μL). Rapid stirring was begun, and a solution of $\text{Y}[\text{N}(\text{TMS})_2]_3$ (50 mL, 0.1 M in toluene) was added. ^1H NMR (500 MHz, CDCl_3): δ 1.36–1.44 (m, 3H), 3.54–3.62 (m, 1H), 3.78–3.86 (m, 1H), 3.98–4.06 (m, 1H), 4.20–4.36 (m, 2H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 172.97, 75.14, 75.11, 75.06, 75.03, 67.91, 67.87, 63.95, 63.88, 18.82, 18.81 ppm. FTIR (NaCl plates, thin film): ν 2986, 2941, 2879, 1744, 1451, 1375, 1271, 1201, 1125, 1046, 963, 863, 753 cm^{-1} .

Variable Temperature Polymerization of MDO. All glassware used was treated as in the previous section. Solution polymerizations of MDO were performed at –30, 0, 20, 40, and 60 °C according to the following example procedure. A 1 mL volumetric flask was charged with MDO (0.435 g, 3.75×10^{-3} mol) and a solution of BnOH in toluene (75 μL of a 1.0 M solution; 7.5×10^{-5} mol). The flask was then filled to the mark with toluene, stirred, and transferred to a vial equipped with a sidearm. The sidearm was sealed with a new septum, and the vial was mounted and sealed on a ReactIR 4000 probe. The probe assembly was then removed from the glovebox and mounted on the instrument. The vial was immersed in a temperature-controlled bath of methanol, ice/water, or silicon oil, depending on the temperature used. The temperature was allowed to equilibrate for 5 min, at which point $\text{Y}[\text{N}(\text{TMS})_2]_3$ (250 μL of a 0.1 M toluene solution; 2.5×10^{-5} mol) was added using a syringe. Monomer bands in the FTIR spectrum at 2984 and 2877 cm^{-1} were observed to verify completion of the reaction. The septum was removed, and a sample taken after a minimum of 1 h after the reaction had reached completion. ^1H NMR spectroscopy was used to determine the percent conversion of the reaction, and the equilibrium monomer concentration was calculated. After the vial was removed from the bath and the solution brought to room temperature, another sample was removed to verify that no further reaction had taken place during the temperature change.

Polymer Blends. A sample of PMDO previously synthesized at –30 °C by precipitation from cold pentane (50 mL) and annealing at 90 °C for 3 h (268 mg, $M_N = 4.6$ kg/mol, PDI = 2.55) was used. PLA was synthesized by addition of a solution of BnOH in THF (8 μL of a 1.0 M solution; 8×10^{-6} mol) and a solution of $\text{Y}[\text{N}(\text{TMS})_2]_3$ in THF (25 μL of a 0.1 M solution; 2.5×10^{-6} mol) to a solution of DL-lactide in THF (4 mL of a 1.0 M solution; 4×10^{-3} mol), followed by precipitation of the polymer (after 30 min) from excess cold MeOH and annealing at 90 °C for 3 h (500 mg, $M_N = 38.3$ kg/mol, PDI = 1.64). Solutions of PMDO and PLA (~250 mg in 3.5 mL of CDCl_3) were then admixed to yield solutions of approximately the desired proportions. Exact weight fractions were verified by ^1H NMR spectroscopy before solvent removal and annealing at 80 °C in vacuo for 2 h. Once loaded into the DSC, samples were heated to 100 °C for 10 min and then cooled to –50 °C

at a rate of 10 °C/min, where the temperature was held for 1 min before heating to 80 °C at a rate of 10 °C/min. The glass transition temperature (T_g) was determined from the second heating scan by a mathematical averaging method. Straight lines were fit tangent to the heat flow curve before and after the transition. From the average of the slopes and intercepts of these two lines, a third line was obtained; T_g was taken as the temperature at which the heat flow curve intersected this third line.

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Supporting Information Available: ^1H NMR spectrum of PMDO (Figure S1) and a sample DSC trace for a PMDO/PLA blend (Figure S2). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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