

Blends of Poly(ϵ -caprolactone-*b*-lactic acid) and Poly(lactic acid) for Hot-Melt Applications

Mikael Stolt,^{1,2} Mikko Viljanmaa,^{3,4} Anders Södergård,^{1,5} Pertti Törmälä⁴

¹Hycail B.V., Industrieweg 24-1, 9804 TG Noordhorn, The Netherlands

²Åbo Akademi University, Laboratory of Polymer Technology, Piispankatu 8, 20540 Turku, Finland

³Kiilto Oy, P.O. Box 250, 33101 Tampere, Finland

⁴Tampere University of Technology, Institute of Biomaterials, P.O. Box 589, 33101 Tampere, Finland

⁵Turku Center for Biomaterials, Itäinen pitkäkatu 4 B (PharmaCity), 20520 Turku, Finland

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ABSTRACT: The condensation reaction product of poly(lactic acid) (PLA) and a hydroxyl-terminated four-armed poly(ϵ -caprolactone) (PCL) was studied by size-exclusion chromatography, DSC, and NMR. The use of both L-lactic acid (LLA) and *rac*-lactic acid (*rac*-LA) was studied and the use of two different catalysts, stannous 2-ethylhexanoate [Sn(Oct)₂] and ferrous acetate [Fe(OAc)₂], was also investigated. The thermal stability and adhesive properties were also measured for the different formulations. The characterization results suggested the formation of a blend of PLA and a *block*-copolyester of PLA and PCL. The results further indicated partial miscibility in the amorphous phase of the blend showing only one glass-transition temperature in

most cases, although no randomized structures could be detected in the *block*-copolymers. The polymerization in the Fe(OAc)₂-catalyzed experiments proceeded slower than in the Sn(Oct)₂-catalyzed experiments. The discoloring of the polymer was minor when Fe(OAc)₂ was used as catalyst, but significant when Sn(Oct)₂ was used. The ferrous catalyst also caused a slower thermal degradation. Differences in the morphology and in the adhesive properties could be related to the stereochemistry of the poly(lactic acid). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 196–204, 2004

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INTRODUCTION

Polymer materials have a unique position in the industrialized world because of their wide range of properties, which are well demonstrated by the use in products for very different purposes and under extremely different conditions. The main part of the polymers, however, is often used only for a short period of time before being discarded. In these short-term applications (bio)degradable polymers (e.g., aliphatic polyesters containing lactoyl units) have been considered to have a potential in a diversity of applications since the advantages from their use in medical applications became apparent.¹ The increased attention has been extensively documented by a large number of review articles published within the last few years.² Linear polyesters based on only lactoyl repeating units have a quite limited field of applications because of the stiffness and brittleness of the polymer. Different approaches have been applied to modify the physical properties and thus broaden the applicability of these polyesters, for example, by copolymerization³ and/or blending⁴ with ϵ -caprolactone.

Lactic acid-based polymers (PLA) were initially prepared by direct polycondensation, but the equilibrium between the reaction components does not favor a high molar mass of the polymer, although some progress has been achieved by using organic solvent,⁵ multifunctional branching agents,⁶ or by sequential melt/solid polycondensation.⁷ The ring-opening polymerization (ROP) route has therefore been most commonly applied, especially when a high molar mass PLA or tailor-made copolymers having specific properties are desired. The ROP route, however, suffers from the drawback of several reaction steps, usually including excessive purification of intermediates, thus lowering the economical viability of the PLAs. The manufacturing of lactic acid-based polymers accordingly must be cost competitive with that of nonbiodegradable polymers if the PLAs are intended for large-scale bulk applications. In applications where low molar mass polymers are desired the polycondensation thus seems more attractive, although the reaction often lacks the controllability found in the ROP route.

Adhesives belong to a special category of polymers frequently used in combination with fiber-based materials (e.g., cardboard and paper). The most commonly used adhesives in packaging materials are hot-melt adhesives⁸ that are applied in the molten state and solidify at room temperature, upon which the adhesive bond is formed. Hot-melt adhesives provide

Correspondence to: M. Stolt (m.stolt@chem.rug.nl).

several advantages such as rapid setting times and the absence of volatile organic compounds.⁹ Traditionally, these hot-melt adhesives are low molar mass materials based on nonbiodegradable polymers such as ethylene vinyl acetate (EVA). Process problems related to nondegradable adhesives have become more apparent as increased recycling of pulp and paper has become a global trend in the paper industry.¹⁰ Another issue is the use of the combination of noncompostable and compostable packaging materials, which is not favorable with respect to composting.¹¹

The use of degradable lactoyl- and caproyl-based polymers as hot-melt adhesives has, to our knowledge, been described only to a limited extent. Some previous studies have reported on the use of L-lactic acid-based polymer formulations in hot-melt applications¹² as well as on the compostability and hydrolytic stability¹³ of such copolyester formulations, although the chain structure of the polymers is not discussed in these papers. This investigation focuses on the characterization and relationship between the composition and the properties of this type of formed polyester formulations.

EXPERIMENTAL

Materials

The *rac*- and L-lactic acids used in the polycondensations were 88% aqueous solutions purchased from Purac B.V. (The Netherlands). The following products were used as received without any further treatment: stannous 2-ethylhexanoate (Tegokat 129, Goldschmidt GmbH, Germany), ferrous acetate (99.5% purity; Aldrich, Milwaukee, WI), and hydroxyl-terminated star-shaped poly(ϵ -caprolactone) (PCL) with a pentaerythritol core (a development product from Solvay Interlox Ltd., Poole, UK). The reference material in the hot tack measurements, a commercial EVA-based packaging hot-melt adhesive (Sitomelt 1525), was supplied by Kiihto Oy (Finland). The two different cardboard materials used for adhesive strength measurements of the hot-melt samples, one consisting of pure cellulose pulp (kraft board) and the other of a clay-coated surface side with poly(lactide) laminated backside (laminated cardboard), were supplied by Ahlstrom (Finland) and Stora Enso (Finland), respectively. All solvents used were of p.a. grade.

Synthesis

The lactic acid containing free water and 0.2 wt % of catalyst were charged to a 1-L round-bottom flask and heated under stirring in a laboratory rotary evaporator unit under a slightly reduced pressure to remove the free water from the reaction mixture and oligomerize the lactic acid. After the calculated free water was

removed and some oligomerization had occurred, the water-receiving flask was emptied and dried, the pressure again lowered stepwise to 30 mbar (avoiding excessive boiling), and the polycondensation reaction continued at 180°C until a number-average molar mass (M_n) of 1000–2000 was obtained for the poly(lactic acid). After this the star-shaped poly(ϵ -caprolactone) was added and the polycondensation continued for 4 h at 185°C. All characterizations were performed on as-polymerized materials. Standard laboratory precautions regarding air- and moisture-sensitive chemicals were used in all chemical handling.

Size-exclusion chromatography (SEC)

Molar mass [M_n (SEC)] and polydispersity index (M_w/M_n) were determined with a size-exclusion chromatograph equipped with an Agilent 1100 isocratic solvent pump, Agilent 1100 autosampler, two PL gel Mixed D linear columns connected in series (Polymer Laboratories Ltd., The Netherlands), and an Agilent 1100 refractive index detector (Palo Alto, CA). All samples were analyzed at room temperature, and polystyrene standards were used for the calibration. The eluent chloroform was delivered at a flow rate of 0.8 mL/min. The samples were dissolved in chloroform at a concentration of 8 mg/mL, and the volume of the injected sample was 25 μ L. Mark-Houwink constants used for generating the universal calibration curve from narrow M_w/M_n polystyrene standards were for polystyrene: $K = 4.9 \times 10^{-5}$, $\alpha = 0.794$; and for poly(lactic acid): $K = 5.49 \times 10^{-4}$, $\alpha = 0.639$.

Differential scanning calorimetry

Differential scanning calorimetric (DSC) measurements were performed on a Perkin-Elmer DSC Pyris 1 calibrated with indium (Perkin Elmer Cetus Instruments, Norwalk, CT). The measurements were performed in the range of -50 to 200°C , at a heating rate of $10^\circ\text{C}/\text{min}$ and a cooling rate of $10^\circ\text{C}/\text{min}$. Glass-transition temperatures (T_g), melting temperatures (T_m), and crystallinity data (ΔH_m) were determined from the second heating period.

NMR spectroscopy

For NMR spectroscopy measurements, the samples were dissolved in chloroform-*d* in 5-mm NMR tubes at room temperature. ^1H -NMR spectra were recorded on a Varian Unity 500-MHz spectrometer (Varian Associates, Palo Alto, CA) and ^{13}C -NMR on a Varian Gemini 200-MHz spectrometer operating at 50.28 MHz. The chemical shifts (δ) given are relative to the residual protons in the chloroform-*d* (7.26 ppm for ^1H and 75.52 ppm for ^{13}C). The ^{13}C data were acquired at a spectral width of 12.5 kHz with an acquisition time of

1.5 s using 1024 repetitions. A relaxation delay of 1 s was used.

End-group titrations

Carboxylic acid end-group titrations were performed on a Mettler Toledo DL53 (Switzerland) using a Mettler Toledo DG 113-SC electrode (1M LiCl/MeOH). A known amount of dissolved sample (~ 0.1 g in CHCl₃) was titrated using a 0.01M KOCH₃/MeOH solution as reagent. Number-average molar mass was calculated based on the acid number after correcting for a blank run.

Weight loss determinations

Weight losses were determined by heating 5-g samples placed in aluminum cups in an oven at 170°C for predetermined times (2, 5, 8, 16, 24, and 31 h), after which the samples were removed from the oven and cooled in a desiccator before gravimetric analysis. All results given are averaged values from two measurements.

Shear strength measurements

Lap shear strengths of the adhesively bonded joints were measured according to the ISO 527 standard by using a Lloyd LR 10 K tensile tester (JJ Lloyd, UK) using a gauge length of 50 mm and crosshead speed of 50 mm/min. The test specimens were prepared according to following method: the adhesives were molten by heating them for 15 min at 160°C and adhesive strips were poured onto the backside of the boards. The surface side of the same board was pressed immediately on the adhesive strip with a roller (weight 3500 g). After the adhesive melt was cooled, the test specimens were cut, giving an adhesive joint of 10 × 30 mm. The measurements were performed at 23°C and 50% relative humidity (RH), after being stored for 4 h at these conditions. The results given are averages from five measurements.

Hot tack measurements

The hot tack measurements were performed on kraft board using an Olinger 105 instrument (California). The tester consisted of a horizontally moving lower sledge and a vertically moving upper sledge. When the test started, the lower sledge moved under a nozzle, which applied the adhesive onto the board. The width of the adhesive strip was 2.0 ± 0.5 mm. The lower sledge continued to move under the upper sledge and, after a fixed time (open time, 0.5 s), the upper sledge was pressed on the lower sledge and the closed time (setting time) was activated. After a predetermined setting time (0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1,

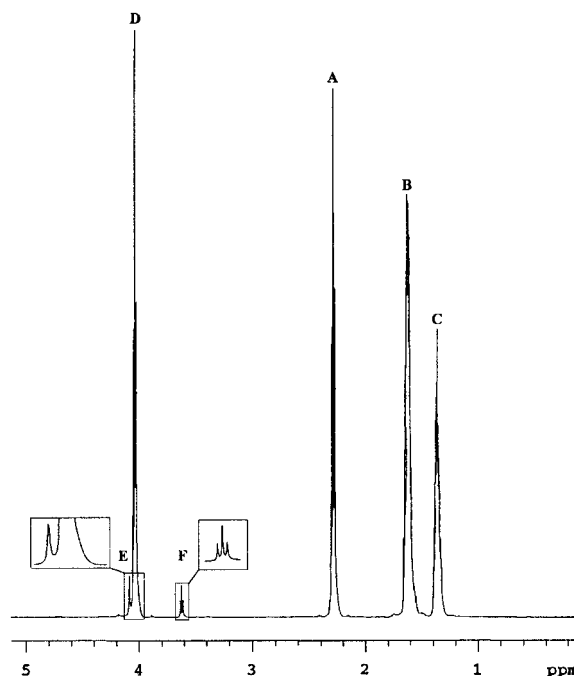


Figure 1 ¹H-NMR spectrum of the star-shaped PCL macroinitiator.

3, and 5 s) the upper sledge moved up and separated the bond. The force to separate the bond was measured with the strain gauge in the instrument (hot tack). The heating temperature and the pressure in the adhesive pot were 160°C and 1 bar, respectively, and the pressure in the vertical cylinder was 0.8 bar. Values given are averages from two measurements.

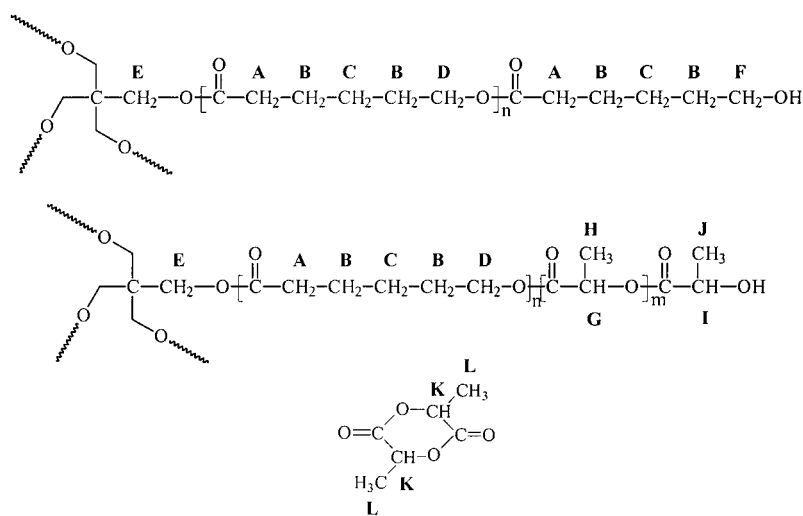
RESULTS AND DISCUSSION

Analyses of the star-shaped poly(ϵ -caprolactone)

In Figure 1 the ¹H-NMR spectrum of the hydroxy end-functionalized star-shaped PCL macroinitiator is seen with the assignments given (A–F) according to Scheme 1. No signal at 3.5 ppm related to pentaerythritol methylenes next to the –OH can be found in the spectrum,¹⁴ indicating quantitative esterification of the initiating alcohol (E at 4.1 ppm). By assigning the F signal at 3.62 ppm as PCL ϵ -methylene next to the –OH end group in accordance with earlier reported assignments,^{3(a),15} a number-average molar mass [M_n (NMR)] of 8800 in close agreement with that of SEC analysis [M_n (SEC) 9000; M_w/M_n 1.14] was obtained. No signals for –OH end-group protons were found in the spectrum.

Analyses of the poly(lactic acid) prepolymers

The ferrous catalyst required somewhat longer polycondensation times than the stannous compound to



Scheme 1 Assignments for the $^1\text{H-NMR}$ spectra in Figures 1 and 2.

achieve similar number-average molar masses (Table I). Furthermore, the optically active L-lactic acid seemed to be slightly more reactive than the racemic counterpart. The reactivity of the different lactic acids should be the same, given that neither stannous 2-ethylhexanoate nor ferrous acetate possesses stereoselective preferences.¹⁶ On the other hand, transesterification reactions have been reported to be more prominent in *rac*-lactide copolymerizations than in L-lactide copolymerizations,¹⁷ which can be a reason for the slower molar mass increase in the **1a** and **3a** polycondensations.

It has been reported that oligocycles, in addition to linear structures, are formed in lactic acid polycondensations under the experimental conditions used in this work.¹⁸ The PLA prepolymers were therefore also analyzed by carboxylic acid end-group titrations. The molar mass of all the samples was consistently about 600 higher when compared to SEC analysis results, confirming that cyclic structures were formed in the polycondensation reactions. A quantification of the different oligocycle species, however, cannot be determined by the analysis methods used. The only quantifiable ring structure, lactide, was formed in 5 mol % yield in all polycondensations, regardless of the catalyst used, because of the temperature-dependent equilibrium concentration.¹⁹

TABLE I
Molar Mass Determinations of the Lactic Acid Prepolymers

PLA	Catalyst	Lactic acid	$M_n(\text{SEC})$	M_w/M_n
1a	$\text{Sn}(\text{Oct})_2$	<i>rac</i>	1100	3.7
2a	$\text{Sn}(\text{Oct})_2$	L	1800	3.1
3a	$\text{Fe}(\text{OAc})_2$	<i>rac</i>	900	2.4
4a	$\text{Fe}(\text{OAc})_2$	L	1400	3.0

Analyses of the hot-melt adhesives

Both the *rac*-lactic acid (**1b**, **3b**) and L-lactic acid (**2b**, **4b**) based hot-melt adhesives prepared showed quite similar polymer characteristics (Table II) regardless of which catalyst was used in the PLA prepolymer synthesis. The only significant catalyst-dependent differences were in the color of the samples, with the stannous 2-ethylhexanoate-catalyzed polycondensations resulting in yellow to brownish polymerization products. The stannous compound is a more efficient esterification catalyst, thus also yielding more side reactions in the equilibrium reaction. One of the byproducts might be an oxidation product generated by the stannous compound, which could give coloration if present in high enough concentration. The amount of the discoloring compound, however, is below the detection limit for the characterization methods used. The ferrous acetate, on the other hand, yielded clear and transparent polymers. The same trends in appearance, contrary to iron-catalyzed ring-opening (co)polymerizations of lactide,²⁰ were also previously observed in preparation of lactic acid-based poly(esterurethane)s with iron carboxylates.²¹

The number-average molar masses determined by end-group analysis [$M_n(\text{NMR})$] were significantly higher than those determined by SEC. Furthermore, the $M_n(\text{SEC})$ results are also considerably lower than would be expected when taking into account the M_n of the star-shaped PCL macroinitiator. The Mark-Houwink (M-H) constants used for the calibration of the SEC were for linear PLA, which could lead to highly erroneous $M_n(\text{SEC})$ values for the copolymers. The discrepancy to $M_n(\text{NMR})$ is of such a magnitude that it would be improbable to be dependent solely on the M-H constants. However, to rule out the possibility of the discrepancy in molar mass being purely an error in

TABLE II
Polymer Characteristics for the Hot-Melt Adhesives Prepared by Polycondensation

PLA	$M_n(\text{SEC})$	M_w/M_n	$M_n(\text{NMR})^a$	Yield (%)	$M_n(\text{NMR})^b$	CL ^c (mol%)	T_g (°C)	$T_m/\Delta H_m$ (°C)/(J/g)
1b	1900	4.5	18,600	45	1900	18	6 ^d	— ^e
2b	3500	4.4	22,900	49	3200	15	22	150/21
3b	1500	4.5	16,300	36	1400	18	6 ^d	— ^e
4b	2400	4.3	16,000	46	2400	15	21	149/21

^a When assuming a well-defined four-armed *block*-copolymer.

^b Yield-corrected values.

^c Caproyl units versus lactoyl units in the polymer blend.

^d A small additional T_g at about 48°C detected in some cases.

^e No melting point detected.

SEC calibration, well-defined star-shaped copolymers of both P(CL-*b-rac*-LA) and P(CL-*b*-LLA) of different molar masses were prepared by sequential ROP (M_n ranging from 9000 to 25,000; M_w/M_n 1.1 to 1.2). All these copolymers showed close agreement in M_n values determined by the different methods, with the $M_n(\text{SEC})$ consistently slightly higher than $M_n(\text{NMR})$.

The results from the ROPs showed that the low $M_n(\text{SEC})$ values obtained for the P(CL-*b*-LA) prepared by polycondensation cannot be attributed solely to SEC calibration errors, suggesting either no linking reaction in the second polycondensation step or that blends of PLA and P(CL-*b*-LA) were obtained. The quantitative reaction of PCL is evident according to ¹H-NMR spectra because no F signal was found in any of the 1b–4b samples and a new signal at the lower field (~4.1 ppm), related to the PCL ϵ -methylene next

to a lactoyl, appeared (Fig. 2). The SEC chromatograms shown in Figure 3 also support the assumption that a linking reaction indeed took place in the second polycondensation step. The elution time for the P(CL-*b*-LLA) (2b) sample is shorter (i.e., higher molar mass) than that for a pure blend of PLLA (2a) prepolymer and PCL. The higher molar mass of the 2b sample compared to that of the PLA prepolymer is of course partly attributed to further homopolymerization of the PLA as a result of the prolonged reaction time. However, the obtained high molar mass fraction is improbable to achieve without any linking reactions with the PCL in the short polycondensation time (4 h) used. A further indication of a successful linking reaction is also shown by the increased polydispersity index ($M_w/M_n = 4.4$). However, the overall increase of M_n is low in the second polycondensation step because of a

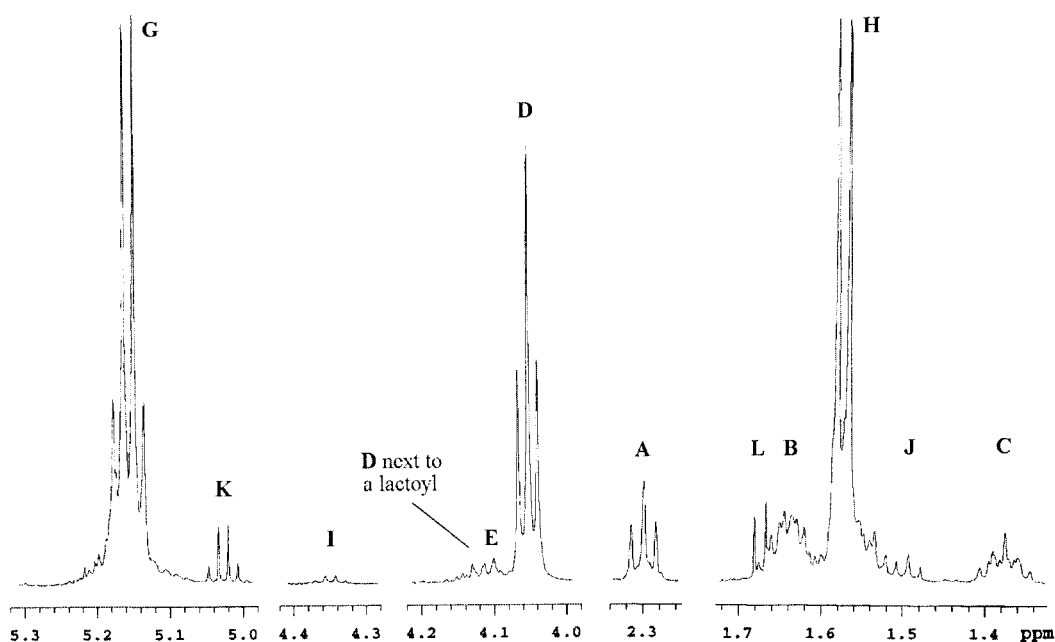


Figure 2 ¹H-NMR spectrum of a typical hot-melt adhesive (2b) prepared by polycondensation. (The peaks are not in correct relation to each other because of different enlargements.)

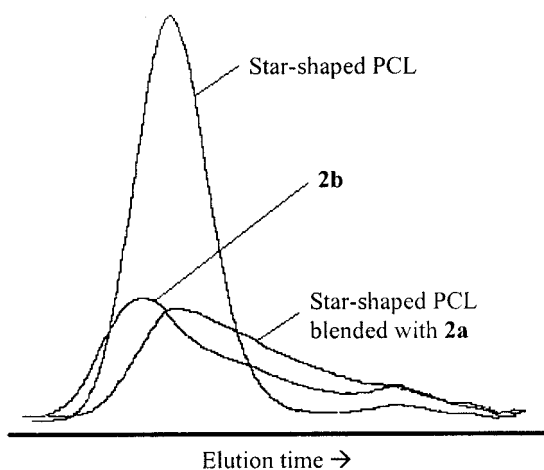


Figure 3 SEC chromatograms of species present in the **2b** sample.

significant fraction of low molar mass polymer present in the sample, which shows that a blend of PLLA and star-shaped P(CL-*b*-LLA) was obtained.

The $^1\text{H-NMR}$ chemical shift of the lactoyl methine end groups (**I**) cannot be separated for the different species present in the blend, which results in too high $M_n(\text{NMR})$ values (Table II, column 4) if one assumes a well-defined four-armed *block*-copolymer. The blend ratio and M_n of the samples can still be estimated by $^1\text{H-NMR}$ using a somewhat simplified model. Because no **F** signals are present in the spectra one can make the initial assumption that all end groups in the *block*-copolymers consist of **I**. Given that the M_n of the PCL block is known [$M_n(\text{NMR})$ 8800] the theoretical number of end groups in the *block*-copolymer is also known. The percentage lactoyl end groups chemically bound to the copolymer (i.e., yield in the second polycondensation step) can then be calculated. When considering this yield in the linking reaction and further assuming that there are only two species present in the blend (i.e., linear PLA of a certain length and star-shaped PCL linked with one linear PLA per arm), number-average molar masses with a better agreement to $M_n(\text{SEC})$ can be calculated using the standard equation²²:

$$M_n = \frac{\sum_{i=1}^N h_i}{\sum_{i=1}^N (h_i/M_i)}$$

where M_i is the molar mass of the individual PLA and P(CL-*b*-LA) species and h_i is the percentage of the species. The yield-corrected $M_n(\text{NMR})$ values are seen in Table II (column 6).

Caproyl and lactoyl polymers have on several occasions been reported to be immiscible, showing distinct glass-transition temperatures of the corresponding homopolymer both in blends and *block*-copolymers.^{3(a)-(d),4} Only one T_g could in most cases be distinguished for these hot-melt samples (Table II), indicating randomization in the second polycondensation step. According to $^{13}\text{C-NMR}$ measurements (Fig. 4), however, the polymers consist of block structures with no signal characteristics for random copolymers.^{3(d),3(e),17,23} One explanation for this apparent miscibility might be the low molar mass of the polymer blend, that is, that the PCL chains are so short that they are able to plasticize the amorphous phase of the PLA to some extent. The lower T_g obtained for the *rac*-lactic acid-based hot-melt samples supports this theory. Similar molar mass-dependent behavior was previously observed for poly(hydroxybutyrate) (PHB) blended with PLLA.^{2(a),24} Miscibility in the amorphous phase was reported for the otherwise immiscible PHB/PLLA blends when the PLLA was of a low enough molar mass. Materials based on poly(lactide-*b*-trimethylene carbonate-*b*-lactide) blended with PLA have also been reported to possess a significantly poorer phase separation for trimethylene carbonate blocks of molar mass (M_n) 10,000–20,000 than for polymers with the rubber blocks exceeding 40,000.²⁵

Samples **2b** and **4b**, with semicrystalline PLA incorporated, showed a melting temperature of about 150°C ($\Delta H_m = 21 \text{ J/g}$) for the PLA but no melting peak related to the PCL block could initially be found in the hot-melt samples. Grijpma and Pennings²⁶ showed that the caproyl sequences are able to crystallize in P(CL-*co*-LLA) copolymers having average CL sequences of 5.5, and Tsuji et al.²⁷ reported of an enhanced crystallization of the copolymer upon storage at room temperature. Crystallization of the caprolactone (CL) sequences, however, was not observed by

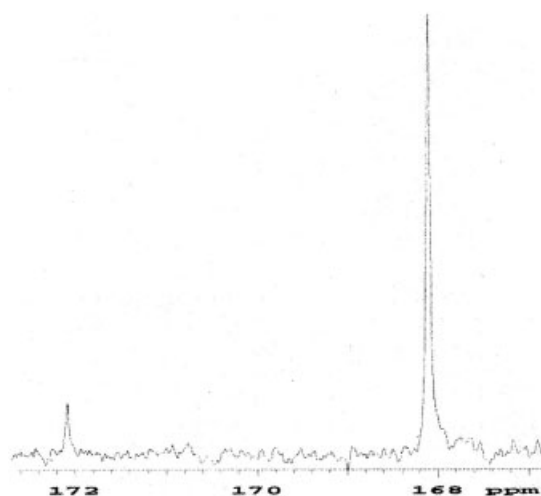


Figure 4 $^{13}\text{C-NMR}$ spectrum of sample **2b**.

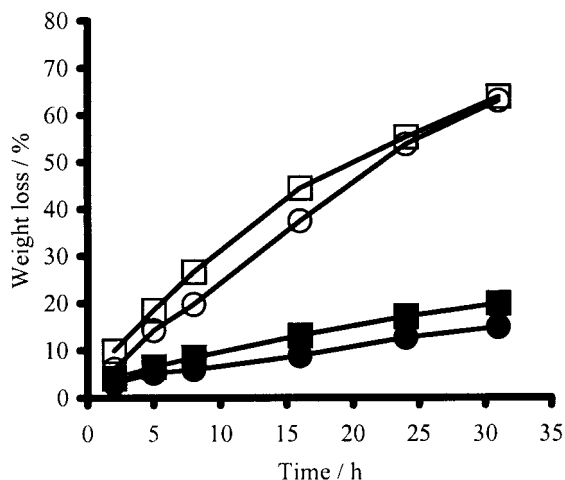


Figure 5 Weight loss of samples **1b** (□), **2b** (○), **3b** (■), and **4b** (●) at 170°C.

the latter group because of a shorter sequence length (3.3). Crystallization of the PCL block in the hot-melt samples is expected because of the long CL sequence (arm length 19.3 caproyl units because no randomized structures could be found) and a melting peak did indeed appear at about 40°C after ageing the polymer at room temperature.

Thermal stability of the hot-melt adhesives

The thermal stability of stannous 2-ethylhexanoate-catalyzed (**2b**) hot-melt samples was previously shown to be insufficient for processing purposes.^{12(a)} The thermal degradation was suppressed by chemical end-group modifications in an additional reaction step by using peroxides or acetic anhydride. Another approach to improve the thermal stability of the polymer is to use a catalyst in the polycondensation reaction that will not cause excessive degradation later when melting the polymer. Iron carboxylates, even though not very efficient catalysts, have been shown to cause only moderate thermal degradation in ROPs of L-lactide at extended polymerization times compared to stannous 2-ethylhexanoate.²⁸ Also for these adhesives the ferrous acetate-catalyzed polymerizations yielded polymers with a considerably higher thermal stability. Figure 5 shows the stability of samples **1b**–**4b** in the form of weight loss as a function of time at 170°C. Only minor differences can be observed between the *rac*- and L-lactic acid-based hot-melt samples, with the racemic having a slightly higher weight loss ratio, which might be related to a higher tendency of transesterification reactions.¹⁷

Adhesive strength of the hot-melt adhesives

Results from the tensile adhesion tests on kraft board and on laminated cardboard can be seen in Figure 6.

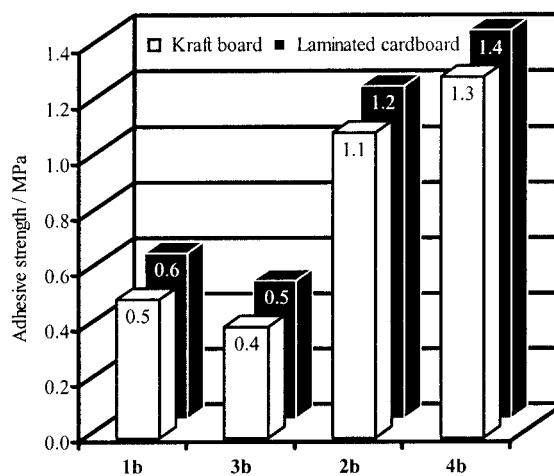


Figure 6 Adhesive strength of the **1b**–**4b** hot-melt adhesives at 23°C and 50% relative humidity.

The adhesion to both boards was good, with the L-lactic acid-based hot-melt samples showing higher adhesion strengths than the tensile strengths of the boards; that is, the values obtained for the **2b** and **4b** samples are actually the strength values of the packaging boards.

However, this was not the case with the *rac*-lactic acid-based samples (**1b** and **3b**). With these formulations, the adhesive layers cracked and the lap shear strength values were fairly low. This behavior is probably attributable to the low T_g (the major T_g at 6°C) in combination with no crystalline domains reinforcing the polymer. An adhesive based on such a material will thus resemble a highly viscous liquid showing a permanent tackiness with a low cohesion strength at the testing conditions (23°C, 50% RH).^{9(a)}

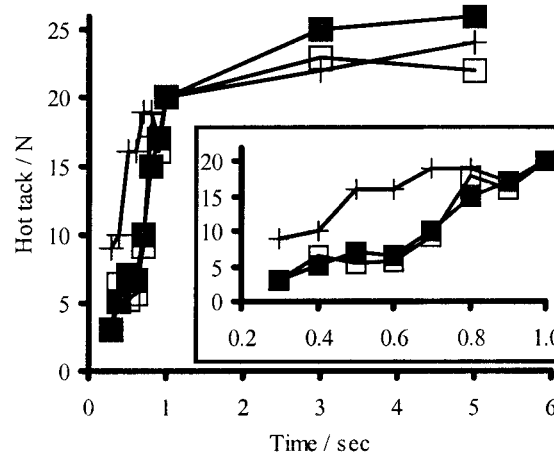


Figure 7 Hot tack development curves for the **1b** (□) and **3b** (■) *rac*-lactic acid-based adhesives in comparison with a commercial EVA-based hot-melt adhesive (+). Enlargement of first second in insert.

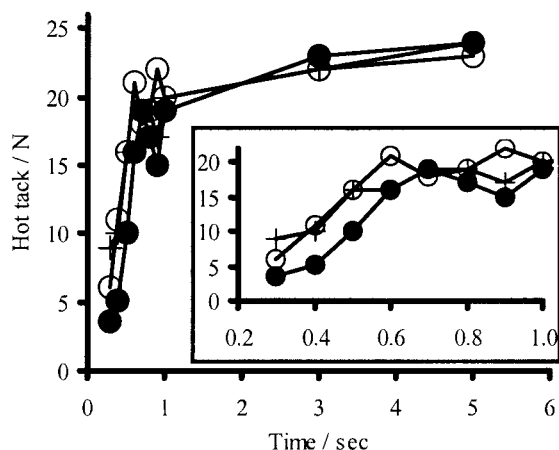


Figure 8 Hot tack development curves for the **2b** (○) and **4b** (●) L-lactic acid-based adhesives in comparison with a commercial EVA-based hot-melt adhesive (+). Enlargement of first second in insert.

Hot tack properties of the hot-melt adhesives

Tack can be defined as a property of a material enabled to form a bond of measurable strength immediately on contact with another surface.²⁹ In the case of hot-melt adhesives tack is measured when the adhesive is in its molten stage (hot tack). For the *rac*-lactic acid-based adhesives (**1b** and **3b**) hot tack values between 0.3 and 0.7 s stayed below 10 N (Fig. 7), attributed to the amorphous nature of the polymers. The hot tack development curve for the **2b** sample, however, was comparable with that of the commercial EVA-based reference material (Fig. 8), and both L-lactic acid-based adhesives, like the reference material, reached over 60% of the final value within just 0.6 s. Force values of about 20 N were obtained in 1 s with all adhesives and there were no significant differences in the end values (5 s). It is worth noting that there was no cohesive failure between the kraft board pieces at these forces. Also, a low pressure (0.8 bar) was used in the vertical cylinder to avoid any compression in the kraft board material to minimize the board effect in the hot tack strength determinations.

CONCLUSIONS

The use of lactoyl- and caproyl-based polymer formulations prepared by polycondensation was studied to correlate the composition and structure to properties relevant in hot-melt adhesive applications. The following main conclusions were established:

1. The studied formulations are blends of poly(lactic acid) and *block*-copolyesters of poly(ϵ -caprolactone) and poly(lactic acid).
2. A slower condensation reaction is obtained by using ferrous acetate, but the catalyst yields a

polymer with significantly less discoloration and better thermal stability compared to a stanous 2-ethylhexanoate-catalyzed formulation.

3. The optical purity of the lactic acid used is crucial for the adhesive properties. The use of racemic lactic acid yielded a tacky adhesive with poor cohesive strength. The adhesive properties of the formulation based on L-lactic acid were similar to those of commercially available EVA-based hot-melt adhesives.

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