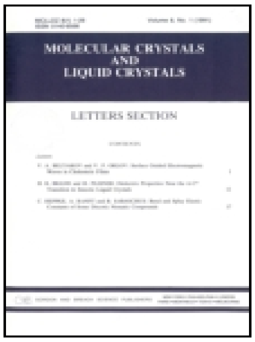

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New Route to Segmental Star-Shaped Copolymers of Lactic Acid

ANITA FRYDRYCH, ZBIGNIEW FLORJAŃCZYK,*
ANNA KUNDYS, AND ANDRZEJ PLICHTA

Faculty of Chemistry, Warsaw University of Technology, Warsaw, Poland

The star-like copolymers containing polylactide core and poly(propylene maleate) arms have been synthesized in two steps. The polylactide segments of M_n in the range 1000–8500 terminated either by OH or COOH functional groups were prepared by melt condensation of L*-lactic acid in the presence of pentaerythritol, or 1,2,3,4-butanetetracarboxylic acid. Selected products were applied as coinitiators and chain transfer agents in the copolymerization of maleic anhydride with propylene oxide catalyzed by magnesium ethoxide or metal salen complexes. Four-arm stars of M_w in the range 11000–35000 have been prepared. Thermal analysis revealed a lower T_g for the copolymers compared to polylactide core.*

Keywords Cyclic anhydrides; epoxides; lactic acid copolymers; segmental polyesters; star polymers

1. Introduction

Polymers based on *L*-lactic acid are one of the emerging groups of polymeric materials produced from renewable resources. Polymers of high molecular weight are commonly manufactured by ring-opening polymerization of the cyclic diester (lactide: 3,6-dimethyl-1,4-dioxane-2,5-dione) which is made by depolymerization of the polycondensed lactic acid. Another approach include the direct condensation of lactic acid using azeotropic dehydration or solid state polycondensation techniques and chain extension reactions of telechelic oligomers with diisocyanates, or other linking agents [1]. The preparation of high molecular weight polymers by conventional bulk polycondensation of lactic acid is not an effective method due to the distillation of lactide and formation of larger cyclic compounds which have a negative influence on the mechanical properties of the final product [2]. Several attempts were made to increase the molecular weight and change the architecture of condensation products by adding the core molecules having three or more hydroxyl or carboxyl groups [3–8]. This strategy give rise to star-shaped poly(lactic acid), however, at large concentration of polyfunctional component one kind of functional group decays in the early stages of the reactions, which limits the further growth of polymer chains. On the other hand, if the polyfunctional compound is used in small amount, the polycondensation product is a mixture of star-shaped and linear molecules of poly(lactic acid). Therefore,

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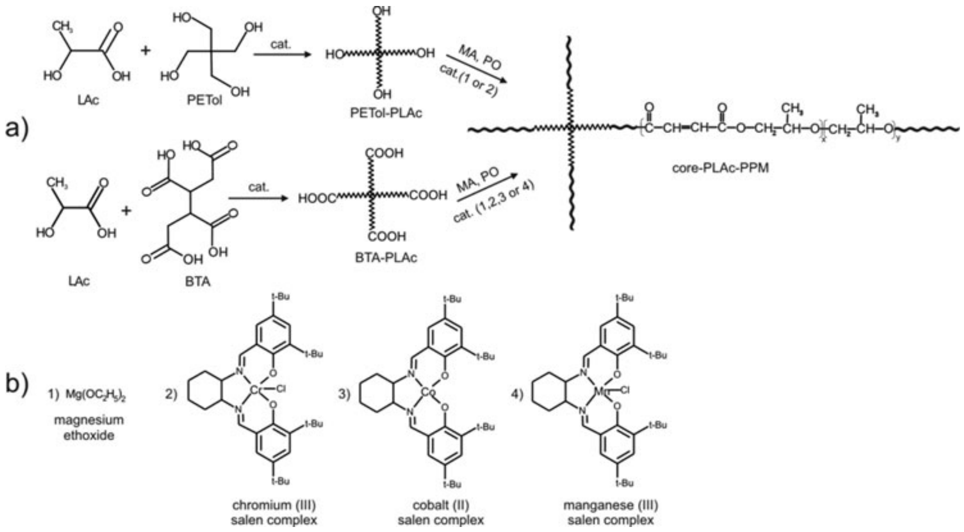
[*] Address correspondence to Zbigniew Florjańczyk, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland. E-mail: evala@ch.pw.edu.pl



Scheme 1. (a) Two-step synthesis of the star-like copolymers of lactic acid and (b) structures of catalysts used in the second step.

the star-like and hyperbranched poly(lactic acid) are typically synthesized by applying catalytic ring opening polymerization of lactide in the presence of polyole of polyamine as core molecule which play the role of coinitiator and/or transfer agent [9–22].

Herein we would like to report the synthesis of star-shaped block copolymers of lactic acids using a similar “core first” approach. The basic new idea is to use stars obtained by polycondensation of lactic acid as a macromolecular-core and extend their arms by more flexible polyester segments made by ring opening copolymerization of maleic anhydride (MA) with propylene oxide (PO) (Scheme 1).

Block copolymers of lactic acid of improved elasticity are the subject of intense studies due to the possibility of their practical application as biomaterials of tailored mechanical properties and rate of biodegradation. Such type of materials were obtained hitherto in reactions of telechelic oligomers of lactic acid and ε-caprolactone [1] or from the catalytic polymerization of lactide in the presence of polyestrodiols [23–26]. Studies on the possibility of applying cheap commodity monomers, like maleic anhydrides and oxiranes for the preparation of elastic segments was the purpose of this work. The synthesis of polyesters *via* catalytic polymerization of these monomers has been studied since 1970s, however, most of the systems reported generally suffer from harsh conditions, low reactivity and low molecular weight of resulting polymers [27]. Renewed interest in these processes was generated in the last decade as a consequence of the development of much more efficient catalysts which allow to produce polyesters at moderate temperature [28–33]. For the purpose of this work we employed mostly magnesium ethoxide and chromium(III) salen complex (Scheme 1) disclosed recently by DiCicio and Coates [32]. We present also some preliminary results which indicate that combination of polycondensation and chain growth polymerization may give simple access to a large family of lactic acid based polymers.

2. Experimental

2.1. Materials

L-Lactic acid (85% aqueous solution), antimony(III) oxide, p-toluenesulfonic acid monohydrate, zinc chloride, tin(II) chloride dihydrate, zinc acetylacetonate monohydrate, zirconium acetylacetonate, magnesium ethoxide, metal salen complexes (Scheme 1b): N,N′-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride, N,N′-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II), N,N′-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride, pentaerythritol (PETol), 1,2,3,4-butanetetracarboxylic acid (BTA), (all of Aldrich) were used without further purification. Propylene oxide (PO, Aldrich) was dried over calcium hydride. Maleic anhydride (MA, Aldrich) was sublimed under reduced pressure. Toluene (POCH) was dried with sodium and distilled. Dichloromethane (POCH) and methanol (POCH) were used without purification.

2.2. Procedures

2.2.1. Preparation of Star-Shaped Poly(Lactic Acid). *L*-Lactic acid (*L*-LAc) aqueous monomer, core compound and catalyst at molar ratio of [LAc]:[core]:[catalyst] = 160:1:0.002, were introduced to a 100 mL two-necked flask, equipped with a magnetic stirrer, a N_2 inlet tube and an outlet to vacuum system connected to the condenser and the cold trap. All oligomers were prepared by melt polycondensation of *L*-lactic acid with multifunctional compounds. The reaction was carried out at 190°C for 8 h. In the first step, run under nitrogen for 1 h, water was continuously distilled off as the reaction by-product. In the second step, run for 7 h, the pressure was slowly reduced to 10^{-2} mbar with removal of water, lactide and low molecular weight oligomers. The remaining mixture was cooled to room temperature and then dissolved in methylene chloride and precipitated from methanol. The resulting condensation oligomeric product was dried in a vacuum oven to constant weight.

2.2.2. Preparation of Copolymers. Condensation products prepared as described in 2.2.1., MA, PO and catalyst (molar ratio of [MA]:[PO]:[macrocore]:[catalyst] = 200:200:1:1) were placed in a tybular glass reactor equipped with a magnetic stirrer. Ring-opening copolymerization of MA with PO in the presence of condensation oligomers was catalyzed by magnesium ethoxide (1), chromium(III) salen complex (2), cobalt(II) salen complex (3) or manganese(III) salen complex (4). The reaction was carried out at 80°C for 15 h in bulk or in toluene solution. The polymerization products were isolated and purified in a similar manner as the starting oligomers.

2.3. Measurements

^{1}H NMR measurement was performed on Varian Merkury 400 MHz spectrometer using DMSO-d_6 or $CDCl_3$ as solvent. The molecular weight and molecular weight distribution were determined by GPC using RI detector and PS calibration on a Viscotek TDA 305 apparatus equipped with one guard and two DVB Jordi gel columns (10^2–10^7, linear, mix bed) in CH_2Cl_2 as eluent at 35°C at a flow rate of 1.0 mL/min. MALDI-ToF mass spectrometry was performed on Bruker Daltonics UltrafleXtreme^{TM} instrument. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile was used as MALDI matrix. The DSC measurements were performed using a DSC Q200 V24.2 Build 107 (TA Instruments) apparatus. The first heating run from 0°C to 200°C was performed at a heating rate of 5°C/min in order to study crystallinity, then cooling at the rate of 20°C/min was applied. The second heating run was measured at the rate of 20°C/min to determine glass transition temperatures.

3. Results and Discussion

The prepolymers which were used as a macrocore molecule in ring opening copolymerization were prepared by melt condensation of *L*-lactic acid in the presence of PETol, or BTA as a core molecule. In the final reaction step carried out under reduced pressure, the condensation process was accompanied by distillation of *L*-lactide contaminated by small amounts of meso lactide and short linear oligomers. The amount of the lactide formed depended considerably on the kind of functional groups in the core molecule and type of catalyst. In some systems, e.g. in reactions involving PETol in the presence of tin(II) chloride, lactide constitutes over 90% of all products, and in analogous reactions involving BTA the lactide yield is ca. 40%. However, polymeric products were the main reaction products in a majority of the systems studied (Table 1). These products were additionally purified by dissolution in methylene chloride and precipitation from methanol.

Table 1. Characterization of condensation products[a]

No.	Core symbol[b]	Catalyst	Yield[c] (%)	$M_{n,HNMR}$[d] (kg/mol)	$M_{n,GPC}$[e] (kg/mol)	$M_{w,GPC}$[e] (kg/mol)	M_w/M_n[e]	x_{PLLA}[f] (mol%)
1	PETol	—	81.5	4.3	0.9	4.8	5.2	49
2		antimony(III) oxide	30.3	3.5	4.7	14.7	3.1	9
3		p-toluenesulfonic acid monohydrate	86.0	5.3	2.2	10.8	4.9	28
4		zinc chloride	39.1	3.9	5.0	11.1	2.2	18
5		zirconium acetylacetonate	53.1	6.0	3.8	14.4	3.8	2
6a		zinc acetylacetonate monohydrate	65.3	7.3	6.7	14.3	2.1	1
6b[g]		zinc acetylacetonate monohydrate	42.6	4.2	4.2	9.7	2.3	15
7a	BTA	zinc acetylacetonate monohydrate	59.4	6.7	8.0	15.8	2.0	16
7b[g]		zinc acetylacetonate monohydrate	62.0	6.6	4.3	14.0	3.2	18
8a		tin(II) chloride dihydrate	58.9	8.1	8.6	23.5	2.7	6
8b[g]		tin(II) chloride dihydrate	64.3	7.1	4.3	23.5	5.5	18

[a] Reaction conditions: [LAc]:[core]:[catalyst] = 160:1:0.002, t = 8h, T = 190°C, p = 10^3-10^{-2} mbar. [b] Abbreviation of cores: PETol: pentaerythritol, BTA: 1,2,3,4-butanetetracarboxylic acid. [c] Yield of crude product. [d] Estimated on the basis of ^{1}H NMR spectra (methine end-groups method). [e] Calculated by means of GPC with polystyrene calibration. [f] Molar fraction of linear poly(lactic acid) chains in the system. [g] Reactions carried out in a greater batch.

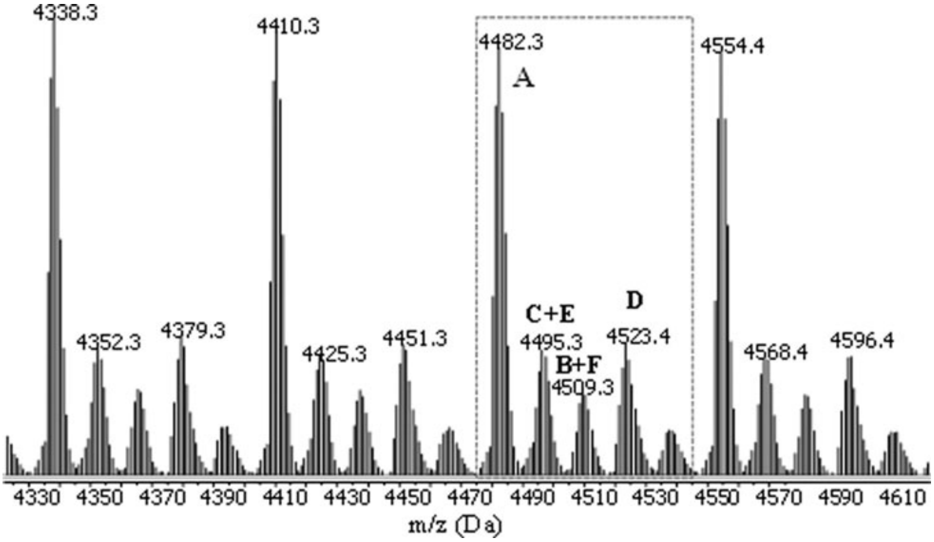


Figure 1. Fragment of MALDI ToF spectrum of condensation product (Table 1, no. 6b).

MALDI ToF spectrum of purified polymer (Fig. 1) clearly indicates the presence of star-shaped molecules (A-sodium adduct, C-potassium adduct) as well as linear chains (B-sodium adduct, D-potassium adduct) which are not attached to the core molecule. In some samples the signals that can be assigned to cyclic lactic acid oligomers (E-sodium adduct, F-potassium adduct) were also observed, however, their population is very low.

In order to determine the content of linear poly(lactic acid) chains, we examined the ^{1}H NMR spectra of the star-like condensation products and pure linear poly(lactic acid). As seen from Fig. 2(a), the spectrum of linear polymer recorded in DMSO-d_6 reveals clear set of signals characteristic for two kinds of terminal unit. For units terminated with a hydroxyl group, three clearly shaped groups of signals are present ($\delta = 5.5$ OH, 4.2 CH and 1.3 ppm CH_3), and for monomeric units terminated with a carboxyl group–two groups ($\delta = 13.2$ COOH and 4.95 CH), whereas the methyl group signal overlaps with the signals of these protons in other monomeric units [34]. In pure polymers of star-like structure only one type of terminal groups should occur, the same as in the applied core molecule. However, always residual signals occurred in spectra of isolated condensation products, characteristic for the second type of terminal groups (Fig. 2(b) and 2(c)).

The mol% of poly(lactic acid) chains not attached to the core molecule was estimated on the basis of the relative intensity of terminal groups signals (Table 1). It appeared that in the systems studied the type of catalyst used has an essential effect on the linear chains content. In non-catalyzed reactions their content may reach even nearly 50 mol%, whereas in reactions carried out in the presence of certain zinc or tin compounds of moderate acidic properties their amount can be reduced to $1-18\%$ (Table 1). The ^{1}H NMR technique was applied also for estimation of M_n, by end-group analysis method and these results were verified by GPC measurement. The differences between these two techniques usually did not exceed 30% of chromatographic data, except for samples of high concentration of linear chains, which were characterized by broad M_w/M_n (Table 1, nos. 1,3). The value of $M_{n\,GPC}$ varied in the range of 1000–8500.

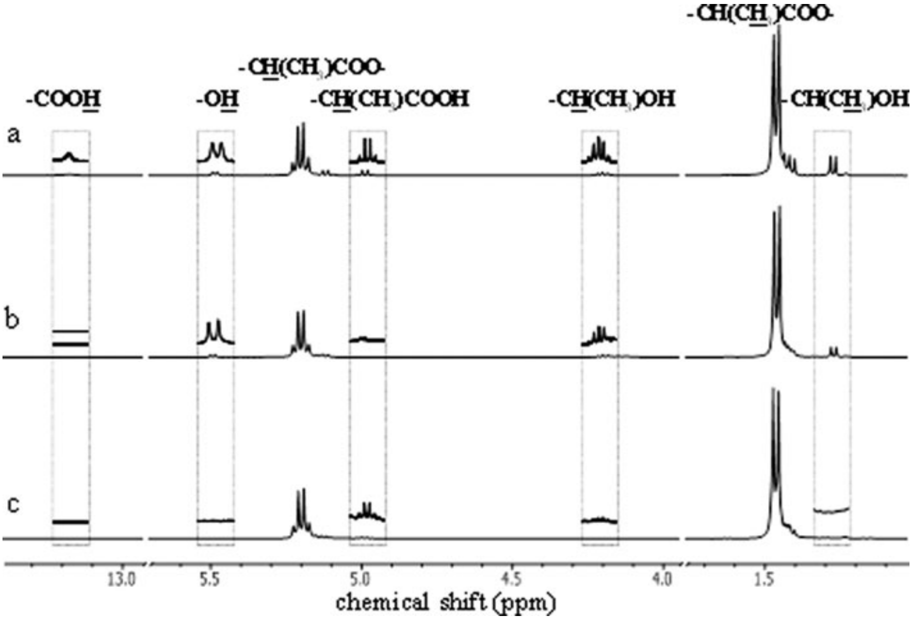


Figure 2. ^{1}H NMR spectra of the condensation products: (a) linear oligomer, (b) star-like oligomer terminated by hydroxyl groups (Table 1, no. 6a) and (c) star-like oligomer terminated by carboxyl groups (Table 1, no. 8a).

In order to obtain segmental copolyesters, ring opening copolymerization of MA with PO was carried out in the presence of condensation products and organic derivatives of Mg, Cr, Co and Mn as catalyst (Table 2).

The syntheses were performed either in bulk or in toluene solution at 80°C. High monomer conversions, in the 60–90% range were achieved under these conditions after 15 h of reaction. The ^{1}H NMR studies of the reaction products revealed the presence of poly(lactic acid) core (δ = 5.2 CH, 1.45 ppm CH_3), poly(propylene maleate) (PPM) monomeric units (δ = 6.4 CH=CH, 5.1 CH, 4.2 CH_2 and 1.2 ppm CH_3) and weak signals attributed to PO homosequences (δ = 5.0 CH, 4.0 CH_2 and 1.05-1.15 ppm CH_3) (Fig. 3). Weak signals attributable to protons in terminal carboxyl groups (δ = 13 ppm) also occur in these spectra, however, the signals characteristic for terminal group in the macrocore were not present, which suggests that condensation products were totally incorporated into the chains composed from oxirane and anhydride monomeric units.

Figure 4 shows the examples of GPC traces of two reaction products. Most of them (Table 2) revealed bimodal distribution of molecular weights. M_p values (determined according to PS calibration) for high molecular fraction which probably contains mostly star-shaped molecules were in the range 13000–19000 (Table 2). M_p values for the second fraction were 3–5 times lower which suggests that the main component of this fraction were linear chains not attached to the macrocore. In some systems these fractions are not clearly separated and GPC curves were monomodal but broad (M_w/M_n = 1.7–4.0) and tailed.

As seen from the data presented in Table 2, in reactions carried out in bulk, polymers of the lowest molecular weight dispersity (M_w/M_n = 1.7–2.5, nos. 5, 6) were obtained in systems with a star comprising carboxyl groups and using magnesium ethoxide as initiator. In this system the catalyst may probably relatively quickly exchange ligands with the core

Table 2. Characterization of copolymerization products[a]

No.	Macro core[b]	Catalyst[c]	α_{MA}[d] (%)	ω_{PLLA}[e] (wt.%)	$M_{n,HNMR}$[f] (kg/mol)	$M_{w,GPC}$[g] (kg/mol)	M_w/M_n[g]	$M_{p,GPC}$[g] (kg/mol)	T_g (°C)
1	6b	1	78.5	20.0	20.3	11.2	3.1	18.7 3.4	—
2[h]	6b	1	60.2	52.7	8.1	12.9	1.9	12.8	—
3	6b	2	66.7	23.7	17.1	12.1	3.1	16.2 4.6	12
4[h]	6b	2	82.4	19.1	22.1	23.9	5.5	17.7 6.8	—
5[i]	7b	1	91.3	40.4	16.0	17.1	2.5	14.1	17
6	7a	1	62.1	54.6	12.1	23.8	1.7	19.1	30
7[h]	8b	1	63.3	57.0	12.3	34.5	4.0	18.3	25
8	7b	2	61.7	29.9	21.4	10.9	3.6	13.3 3.8	21
9[h]	8b	2	73.7	51.6	13.6	30.7	2.1	18.6	—
10	7b	3	53.4	48.2	13.4	16.9	3.7	14.8	—
11	7b	4	60.1	53.5	12.2	18.8	2.3	14.2	—
12[j]	7b	1	79.7	25.5	25.1	5.0	4.7	9.4 1.7	–5
13[k]	8b	1	—	37.4	18.7	20.3	7.7	22.8	1

[a] Reaction conditions: [MA]:[PO]:[macrocore]:[catalyst] = 200:200:1:1, t = 15 h, T = 80°C. [b] Numbers correspond to those from Table 1. [c] Numbers correspond to those from Scheme 1b. [d] Conversion of maleic anhydride (MA) calculated from ^{1}H NMR spectra of crude product. [e] Fraction of PLLA in the product. [f] Estimated on the basis of ^{1}H NMR spectra. [g] Calculated by means of GPC with polystyrene calibration. [h] Reaction conditions the same as "a" but toluene was used as a solvent. [i] Reaction conditions the same as "a" but molar ratio of [MA]:[PO]:macrocore]:[catalyst] was equal to 100:100:1:1. [j] Reaction conditions the same as "a" but ethylene oxide was used as an epoxide. [k] Reaction conditions the same as "a" but succinic anhydride was used as an anhydride and T = 150°C.

functional group, which favors the formation of sites on which the star arms grow (Eq. 1).

$$2\,RCOOH + (C_2H_5O)_2Mg \rightarrow (RCOO)_2Mg + 2C_2H_5OH \qquad (1)$$

In a majority of systems the catalyst molecules may probably react also directly with monomers, which leads to the formation of a certain population of macromolecules of linear structure. It can be assumed that the ligand exchange process is much less effective in systems with a star containing secondary hydroxyl groups, which results in bimodal distribution of molecular weights. However, the product molecular weight dispersity can be considerably improved by carrying out the reactions in a toluene solution (Table 2, no. 2). A similar effect was obtained also in reactions with a star comprising carboxyl groups in the presence of chromium(III) salen complex which is regarded as one of the most effective catalyst of maleic anhydride with oxiranes copolymerization [32] (Table 2, no. 9).

The thermal behavior of the blends obtained has been studied by differential scanning calorimetry (DSC). In all cases, no melting transition was detected, in the contrary to macrocore molecules which contained a small fraction of a crystalline phase of melting point 120–130°C. All products reveal one glass transition temperature in the

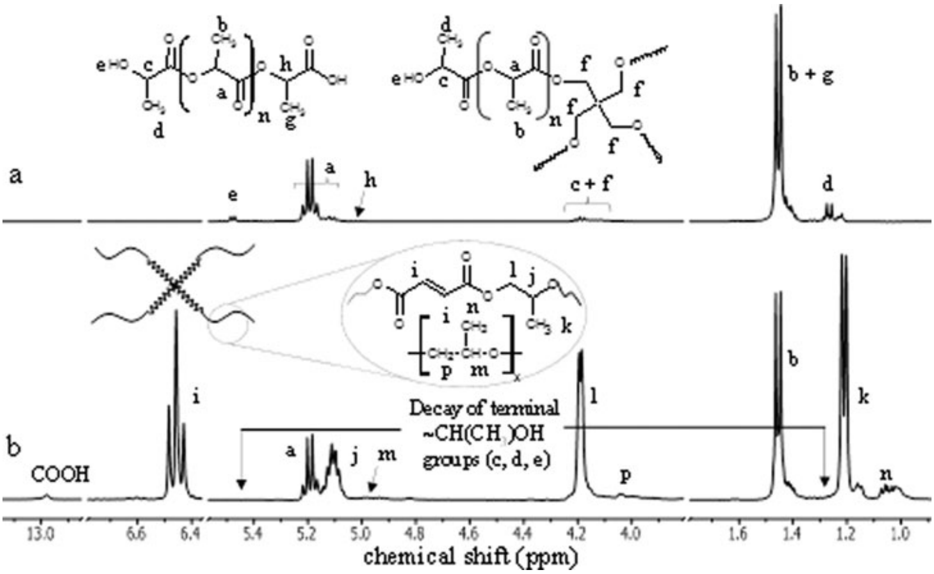


Figure 3. ^{1}H NMR spectra of (a) star-like oligomer terminated by hydroxyl groups (Table 1, no. 6b) and (b) the copolymerization product (Table 2, no. 3).

range 12–30°C depending on the proportion between poly(lactic acid) and poly(propylene maleate) monomeric units (Table 2). Compared to macrocore molecules (T_g around 40 and 60°C for hydroxyl- and carboxyl-terminated stars), the glass transitions were considerably lower for segmental copolymers which is attributed to the flexibilizing effect of poly(propylene maleate) chains which act as internal and external plasticizers (Fig. 5).

We have found that standard *cis-trans* isomerization of maleate units in the presence of diethylamine [35] afforded segmental copolymers containing poly(propylene fumarate) units. After reaction with amine, the signal at 6.25 ppm of the maleate isomer was no longer present, and a new signal at 6.80 ppm was observed, corresponding to the fumarate units. Isomerization caused an increase in the T_g value of the product by approximately 10°C. This process might be of some practical importance because the unsaturated polyesters based on poly(propylene fumarate) were widely explored for biomedical applications [36].

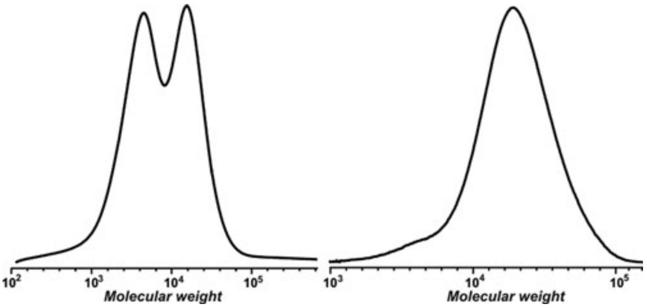


Figure 4. GPC traces of copolymerization products obtained in reactions in the presence of (a) chromium(III) salen complex (Table 2, no. 3) and magnesium ethoxide (Table 2, no. 6).

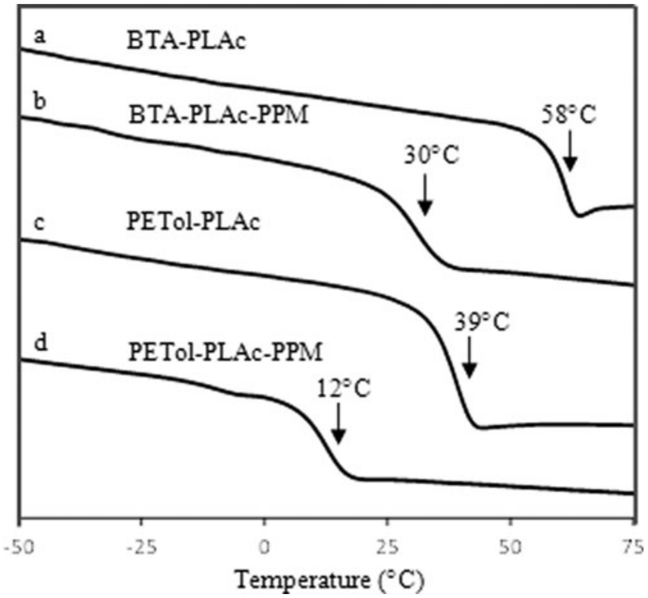


Figure 5. DSC traces of (a) carboxyl-terminated star (Table 1, no. 7a), (b) segmental copolymer (Table 2, no. 6), (c) hydroxyl-terminated star (Table 1, no. 6b), (d) segmental copolymer (Table 2, no. 1).

Preliminary observations showed that the macrocore terminated by carboxyl group used in this work can be also combined with polyesters obtained from catalytic copolymerization of MA and ethylene oxide (Table 2, no. 12) or copolymerization of succinic anhydride with PO (Table 2, no. 13) producing copolymers of T_g below room temperature.

Conclusions

We have shown that star-shaped poly(lactic acid) core could be effectively combined with soft poly(propylene maleate) segments under condition of catalytic copolymerization of maleic anhydride with propylene oxide. The catalysts applied provided high monomer conversion (60–90%) and allowed the obtaining products of relatively high molecular weight ($M_w = 11000–35000$). The molecular weight distribution was often bimodal which suggests that the linking process is not fully selective and the final products constitute the mixture of segmental star-like polymers and linear chains of maleic anhydride–propylene oxide copolymers. However, by the proper selection of catalyst and reaction conditions, the products of M_w/M_n in the range of 1.7–2.1 can be obtained. The copolyesters obtained were amorphous and exhibited one glass transition temperature which was significantly lower than that of poly(lactic acid). The structure of the arms attached to the poly(lactic acid) core can be easily modified by isomerization of maleate units and by using other starting materials in the copolymerization step.

The present studies aim to the utilization of the thus modified poly(lactic acid) as a biodegradable encapsulation material in controlled release system.

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