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Polymer 41 (2000) 3705–3712

polymer

Polystereoisomers of 2-butyl and 3,3-dimethyl-2-butyl malic acid esters: configurational structures/properties relationship

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Received 22 June 1999; accepted 29 July 1999

Abstract

New poly(β-malic acid alkyl esters) with two stereogenic centers have been synthesized by anionic ring-opening polymerization of racemic and optically active 2-butyl and 3,3-dimethyl-2-butyl malolactonates. The configurational structure of these racemic and optically active polyesters has been determined by ^{13}C NMR analysis. Comparison between polydiastereisomers structures has been possible by using this spectroscopic method. Several main-chain and side-chain carbon atoms were stereosensitive, and polystereoisomers composition has been deduced from ^{13}C NMR spectra. Thermal properties of the different polystereoisomers have been correlated with the configuration of both chiral sites in the macromolecular chains. It has been shown, crystallinity rate was dependent on main-chain configurational structure. The lateral stereogenic center is important to increase the organization of macromolecular chains in crystallites and therefore their regularity. Moreover, the presence of the 3,3-dimethyl-2-butyl group led to a semi-crystalline racemic polymer, that confirms the particular behaviour of this bulky group in a macromolecular architecture. Comparison has been done with poly(benzyl 3-alkylmalates) containing two stereogenic centers in the main-chain.

Keywords: Poly(2-butyl β-malate); Poly(3,3-dimethyl-2-butyl β-malate); Configurational structure

1. Introduction

The necessary adjustment of the materials properties for specific applications leads to the macromolecular engineering of synthetic or bioartificial polymers with a large variety of chemical structures and with reproducible characteristics. The presence of stereogenic centers in the macromolecular chain is an important structural factor with regard to conformation, configuration and therefore morphology. Chirality can be used for taking advantage of modifying physical and mechanical properties of polymeric materials as exemplified by lactic acid stereocopolymers [1] applied for different medical devices [2]. In the case of surgical implants, semi-crystallline polymers are necessary for bone repair [3] while for drug delivery systems, racemic amorphous polylactide is used [4]. In the same way, bacterial polyhydroxyalkanoates are very interesting for environmental or biomedical applications due to the presence of only (*R*)-repeating units in the skeleton [5]; this stereoregularity leads to semi-crystalline optically active and biodegradable architectures [6]. Synthetic stereocopolymers of malic acid esters prepared from (*S*)- and (*R*)-aspartic acid [7] or (*S*)- and (*R*)-malic acid [8] yield optically active poly(β-malic acid esters) with a stereoregularity strictly connected with monomer feed enantiomeric excess (≥98%) [9].

For increasing the versatility of the poly(β-malic acid) derivatives family, a second stereogenic center has been introduced with several objectives: polystereoisomers NMR configurational analysis, catalytic enantioselective reactions, drug encapsulation, temporary devices preparation. Two routes have been used:

1. A chiral precursor with two asymmetric carbons leading to main chains combining enantiomers or diastereoisomers, 3-methylaspartic acid, yields poly(β-3-methylmalic acid) [10]. This amino acid can be prepared by biotransformation from mesaconic acid under (2*S*,3*S*) [11] and (2*S*,3*R*) [12] diastereoisomers form, using 3-methylaspartase from *Clostridium tetanomorphum* as enzymatic catalyst; (2*S*,3*S*) 3-ethyl- and 3-isopropyl aspartic acids have been also prepared by bioconversion [13]. In all cases, the amino acid has been transformed in benzyl 3-alkylmalolactonate, before anionic ring opening polymerization [14,15]. The major interest of this synthesis route is the possibility to prepare optically active polymers with repeating units including only one type of configurational structure as determined by ^{13}C NMR.

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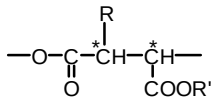
PII: S0032-3861(99)00557-1



R = H, CH_3, C_2H_5, $CH(CH_3)_2$

R' = $CH_2C_6H_5$ or neutral, chiral, reactive, bioactive group

2. The other possibility consists in the introduction of a chiral center in the pendant ester group of the β-substituted β-lactone monomer. A first structure had been build up, starting from 2-methylbutanol as chiral alcohol [16]. Different polystereoisomers had been prepared and characterized [17].

In order to understand better, the relationship between chemical structures of the pendant ester group and thermal properties, two new series of malolactonate stereoisomers with two stereogenic centers have been prepared [18]. In this paper, we report the synthesis of the corresponding polystereoisomers and their configurational structure analysis by ^{13}C NMR. Thermal properties have been compared with others polyesters of the same family containing two stereogenic centers.

2. Experimental

2.1. Chemicals

Stereoisomers of 4-((2-butyl)oxycarbonyl)-2-oxetanone and of 4-((3,3-dimethyl-2-butyl)oxycarbonyl)-2-oxetanone have been synthesized and purified according to the routes described previously [18], starting from malic acid enantiomers and by using (*RS*)-, (*R*)- or (*S*)-2-butanol and (*RS*)- or (*S*)-3,3-dimethyl-2-butanol. The polymerization procedure was the same for all stereoisomers. 120 μl of an initiator solution (tetraethylammonium benzoate) (10^{-3} equiv.) was placed in a flask. Solvent (anhydrous ethanol) was eliminated under vacuum (2×10^{-2} mm Hg) at room temperature. Initiator was dried at room temperature (2 h, 2×10^{-2} mm Hg) and then placed under N_2 atmosphere. A total of 1 g of monomer kept under N_2 atmosphere was transfered in the polymerization flask. Polymerization was carried out at 37°C for six days (disappearance of the lactone band at 1825 cm^{-1} in IR spectroscopy). Polymer, if soluble, was therefore dissolved in acetone and, after HCl addition (1 drop), precipitated in a large excess of ethanol. The sample was dried under vacuum at 40°C for 48 h.

2.2. Analysis

^1H and ^{13}C NMR spectra, in solution ($CDCl_3$), were recorded at 297 K, on a Bruker AC200 spectrometer using 5 mm sample tubes. Solid state ^{13}C NMR spectra were recorded at 297 K, on a 75 MHz Bruker spectrometer. Glass transition temperature (T_g) and melting temperature (T_m) were measured by differential scanning calorimetry using a SETARAM 92 DSC apparatus under normal atmosphere (air) at a heating rate of 10°C mn^{-1}. Molecular weight distributions were determined by size exclusion chromatography (SEC) using a Spectra Physics P100 equipped with three columns of PL-gel (100, 500 and 10^4 Å) and a SHODEX RI-71 refractive index detector, in THF or $CHCl_3$ with a rate of 1 ml min^{-1}.

Polymer P1 (3*RS*,2′*RS*): yield 80%; $T_g = -10$°C; $[\alpha]_D^{25}$ ($c = 1$, THF) = 0; SEC (THF, PS standards) $M_n = 48\,300$, $M_w = 55\,400$, Ip = 1.2; ^1H NMR ($CDCl_3$, δ ppm): 0.82 (broad (br.) peak, 3H, 4′CH_3), 1.15 (br., 3H, 1′CH_3), 1.51 (br., 2H, 6CH_2), 4.82 (m, 1H, 2′ CH), 5.40 (br., 1H, 3CH); ^{13}C NMR ($CDCl_3$ δ ppm): 9.52 (d, 4′CH_3), 19.17 (d, 1′CH_3), 28.57 (d, 3′CH_2), 35.34 (2CH_2), 68.71 (d, 3CH), 74.28 (t, 2′CH), 167.80-168.15 (d, 2 CO).

Polymer P1 (3*S*,2′*S*): yield 55%; $T_g = 34$°C, $T_m = 157$°C, $\Delta H_m^o = 37$ J g^{-1}; SEC ($CHCl_3$, PS standards) $M_n = 42\,000$, $M_w = 66\,000$, Ip = 1.6; ^1H NMR ($CDCl_3$, δ ppm): 0.82 (t, 3H, 4′CH_3), 1.15 (d, $J = 6.2$ Hz, 1′CH_3), 1.51 (m, 2H, 6CH_2), 2.90 (m, 2H, 2CH_2), 4.82 (m, 1H, 2′CH), 5.40 (m, 1H, 3CH); ^{13}C NMR ($CDCl_3$, δ ppm): 9.52 (d, 4′CH_3), 19.17 (d, 1′CH_3), 28.57 (d, 3′CH_2), 35.34 (2CH_2), 68.71 (d, 3CH), 74.28 (t, 2′CH), 167.80-168.15 (d, 2 CO).

Polymer P1 (3*S*,2′*R*): yield 71%; $T_g = 39$°C, $T_m = 179$°C, $\Delta H_m^o = 33$ J g^{-1}; $[\alpha]_D^{25}(c = 1, \text{THF}) = 60°$; SEC (THF, PS standards) $M_n = 56\,100$, $M_w = 82\,000$, Ip = 1.5; ^1H NMR ($CDCl_3$, δ ppm): 0.82 (t, 3H, 4′CH_3), 1.15 (d, $J = 6.2$ Hz, 1′CH_3), 1.51 (m, 2H, 6CH_2), 2.90 (m, 2H, 2CH_2), 4.82 (m, 1H, 2′CH), 5.40 (m, 1H, 3CH); ^{13}C NMR ($CDCl_3$ δ ppm): 9.50 (d, 4′CH_3), 19.15 (d, 1′CH_3), 28.60 (d, 3′CH_2), 35.29 (2CH_2), 68.56 (d, 3CH), 74.28 (t, 2′CH), 167.82-168.09 (d, 2 CO).

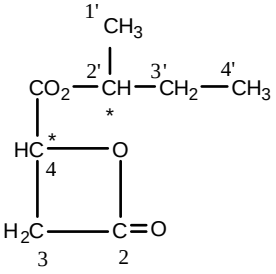
Polymer P2 (3*RS*,2′*RS*): yield 74%; $T_g = 36$°C, $T_m = 180$°C, $\Delta H_m^o = 25$ J g^{-1}; SEC (THF, PS standards) $M_n = 200\,000$, $M_w = 240\,000$, Ip = 1.6; ^1H NMR ($CDCl_3$,(δ ppm): 0.88 (s, 9H, 4′$(CH_3)_3$), 1.15 (d, $J = 6.3$ Hz, 3H, 1′CH_3), 2.99 (m, 2H, 2CH_2), 4.73 (m, 1H, 2′CH), 5.50 (m, 1H, 3CH); ^{13}C NMR ($CDCl_3$, δ ppm): 15 (1′CH_3), 26 (4′CH_3), 34 (3′C), 37 (2CH_2), 68 (3CH), 79 (2′CH), 167 (2 CO).

Polymer P2 (3*R*,2′*S*): yield 99%; $T_g = 143$°C, $T_m = 232$°C, $\Delta H_m^o = 47$ J g^{-1}; insoluble powder; ^{13}C NMR (solid state, δ ppm): 15 (1′CH_3), 26 (4′CH_3), 34 (3′C), 37 (2CH_2), 67 (3CH), 79 (2′CH), 167 (2 CO).

Polymer P2 (3*S*,2′*S*): yield 87%; $T_g = 148$°C, $T_m = 168$°C, $\Delta H_m^o = 39$ J g^{-1}; insoluble powder; ^{13}C NMR (solid state, δ ppm): 15 (1′CH_3), 26 (4′CH_3), 34 (3′C), 37 (2CH_2), 68 (3CH), 79 (2′CH), 167 (2 CO).

Polymer P3 (3*S*,2′*RS*): yield 80%; $T_g = 116$°C, $T_m = 246$°C, $\Delta H_m^o = 43$ J $g^{-1;}$ insoluble powder; ^{13}C NMR (solid state, δ ppm): 15 (1′CH_3), 26 (4′CH_3), 34 (3′C), 37 (2CH_2), 68 (3CH), 79 (2′CH), 167 (2 CO).

Table 1
Characteristics of 2-butyl malolactonates **1**



Lactone: expected configurations	Stereoisomers composition (%)			
	(4*S*,2′*S*)	(4*S*,2′*R*)	(4*R*,2′*S*)	(4*R*,2′*R*)
(4*RS*,2′*RS*)	25	27	26	22
(4*R*,2′*S*)	0	0	93	7
(4*R*,2′*R*)	0	0	4	96

3. Results and discussion

3.1. Polymers formation and configurational structure analysis

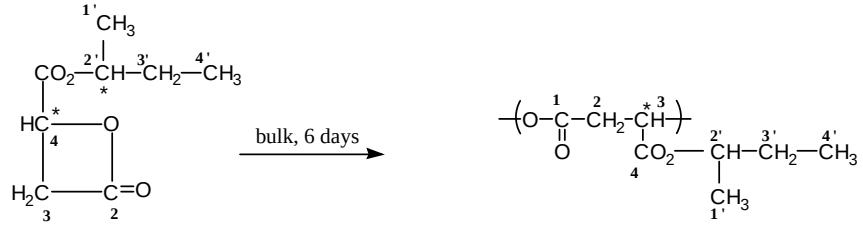
Three 2-butyl malolactonates, **1**, have been prepared according to the malic acid synthesis route [18] and characterized by ^{13}C NMR and chiral gas chromatography (GC). Lactones diastereoisomeric excess has been deduced from these two analytical methods and it has been concluded, no important racemization takes place during the lactone ring formation step and the synthesis is configurations respecting (Table 1). For exemple, **1c**, which was prepared from (*S*)-malic acid and (2*S*)-butan-2-ol, presented almost the sole (4*R*,2′*R*) stereoisomer.

2-Butyl malolactonate stereoisomers, **1**, have been polymerized in bulk at 37°C, using tetraethylammonium benzoate as initiator (Scheme 1: polymerization of 2-butyl malolactonates, **1**).

For the different polymers, the conversion was complete in 6 days. After dissolution in chloroform and precipitation in ethanol, high molecular weights with a relative narrow polydispersity were observed (Table 2). In all polymerization reactions concerning malolactonic acid esters, theorical molecular weights were not obtained due to transfer and termination reactions [19].

According to the structure of the stereocopolymers, effects of tacticity as well as diastereoisomerism could be expected. The configurational structure analysis was carried out by ^{13}C NMR spectroscopy in order to determine the diastereoisomeric composition of the different polymers. Fig. 1 displays the ^{13}C NMR spectrum of **P1** (3*RS*,2′*RS*), prepared from the racemic (4*RS*,2′*RS*) lactone.

Due to the presence of two stereogenic centers in the repeating units and consequently stereosensitivity of several carbon atoms to stereosequences, this spectrum is complex. Assignment of the carbonyl carbon atoms has been made by comparison with the spectrum of poly(2-methylbutyl β-malate) [17]. The peaks corresponding to the main chain 1C and pendant 4C are respectively at 168.15 and 167.75 ppm. 4′CH_3, 2′CH_2 and 1CO are sensitive to diad effects and 2′CH is stereosensitive to triad effects as shown on Fig. 1. Indeed, 1C displays two peaks corresponding to meso and racemic diads and 2′CH, three peaks at 74.20, 74.28 and 74.36 ppm, in the ratio 1/2/1, corresponding to the four triads iso, syndio, heteroiso, heterosyndio. From the expansion of the 2′CH region of the three stereoisomers spectra, it is possible to conclude that **P1** (3*S*,2′*R*) and **P1** (3*S*,2′*S*) contain a very large excess of one type of repeating units and are essentially isotactic (Fig. 2). This result was confirmed by taking into account the 4′CH_3 signals. Two peaks (9.50 and 9.55 ppm) are present in **P1** (3*RS*,1′*RS*) spectrum; on the contrary, only one peak exists at 9.56 for **P1** (3*S*,2′*S*) and one peak at 9.50 ppm in the case of **P1** (3*S*,2′*R*); there is a diastereisomeric relationship between both peaks.



1

a (4RS,2'RS)
b (4R,2'S)
c (4R,2'R)

P1

a (3RS,2'RS)
b (3S,2'S)
c (3S,2'R)

Scheme 1.

Table 2
Characteristics of poly(2-butyl malates) **P1**

Polymer	Yield[a] (%)	Solvent (SEC)	M_n[b]	Ip[b]	M_n calculated	$[\alpha]_D^{25}$[c]
(3*RS*,2′*RS*)	80	THF	38 000	1.3	200 000	0
(3*S*,2′*S*)	55	$CHCl_3$	42 000	1.6	200 000	n.d.[d]
(3*S*,2′*R*)	71	THF	56 000	1.5	200 000	+60

[a] Polymer yield after precipitation.
[b] Determined by SEC with differential refractometer detector and polystyrene standards.
[c] Here $c = 1$ in THF.
[d] Not determined.

At last, this structural analysis shows there is no racemization during the ring-opening polymerization which proceeds with an configuration inversion of the 4C carbon atom [20]. The polymer diastereisomeric composition is identical to the monomer composition. Indeed, two very small peaks are visible on the foot of the signal at 74.28 ppm, in the **P1** (3*S*,2′*S*) spectrum; the diastereisomeric excess of the lactone was 86%. On the other hand, this excess was 92% for **P1** (3*R*,2′*R*) and **P1** (3*S*,2′*R*) and the signal at 74.27 ppm was very fine and unique.

The second lactone series **2** contained the 3,3-dimethyl-2-butyl bulky group as ester group. The stereochemistry of this lactone was more complicated than in the case of **1**. In the malic route synthesis, after the formation of malic acid anhydride by reaction of malic acid with trifluoroacetic acid anhydride, the second reaction concerns the addition of an equivalent of alcohol, leading to one monoester. In the case of 3,3-dimethyl-2-butanol, the reaction was leading to a kinetic resolution and the rate of formation of diastereoisomers **2**(3*R*,2′*R*) and **2**(3*S*,2′*S*) was not identical to the formation rate of diastereoisomers **2**(3*R*,2′*S*) and **2**(3*S*,2′*R*) (Scheme 2: opening of malic acid anhydride by 3,3-dimethyl-2-butanol).

Consequently, the diastereoisomeric excess of the different lactones takes into account this specific effect. This effect can be explained by the presence of a chiral center

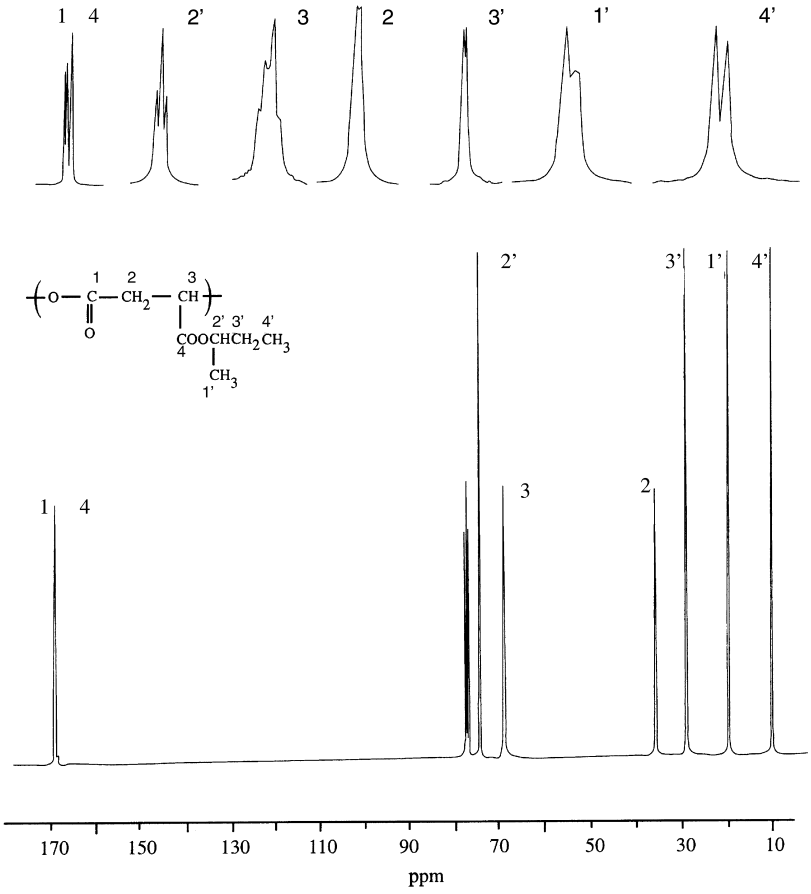


Fig. 1. ^{13}C NMR spectrum of **P1** (3*RS*,2′*RS*) in $CDCl_3$.

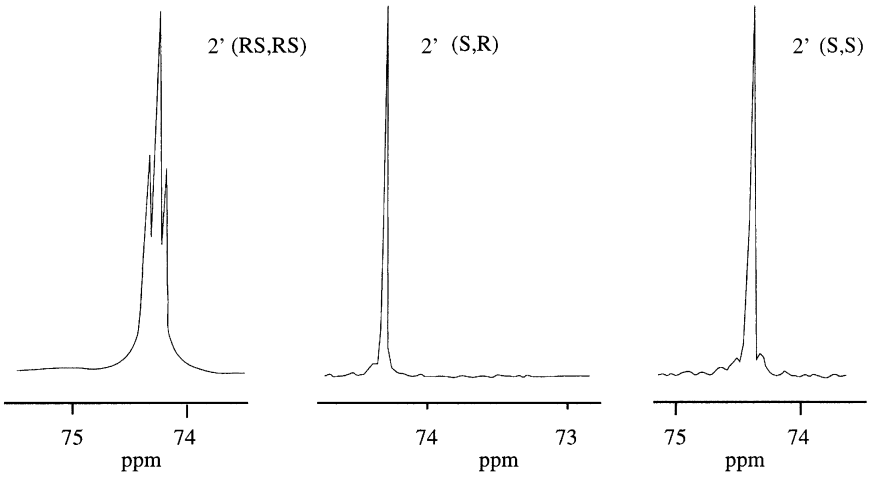


Fig. 2. 2′C carbon atom ^{13}C NMR signals of **P1**.

in malic acid and in the alcohol with a bulky alkyl group which is known to have a particular behaviour in organic chemistry reactions. The four stereoisomers **2** were polymerized according to the same experimental procedure as in the case of **1**. Properties of the resulting polymers **P2** are quite different.

The presence of the 3,3-dimethyl-2-butyl pendant group has induced the insolubility of the optically active polymers. Only, molecular weights of racemic **P2** (3*RS*,2′*RS*) has been determined (Table 3).

The structure of the four polystereoisomers has been studied by solid state ^{13}C NMR. The spectrum corresponding to the racemic polymer **P2** (3*RS*,2′*RS*) is displayed in Fig. 3.

3CH carbon atom is stereosensitive to the configuration of the stereogenic centers. As shown in Fig. 4, optically active polydiastereoisomers **P2**(3*S*,2′*S*) and **P2**(3*R*,2′*S*) displayed a fine single peak centered respectively at 68 and 67 ppm. **P2** (3*S*,2′*RS*) presented a peak at 68 ppm and an uncoupling at 67 ppm; this result is in agreement with the presence of two diastereoisomers as in the monomer feed (Fig. 4).

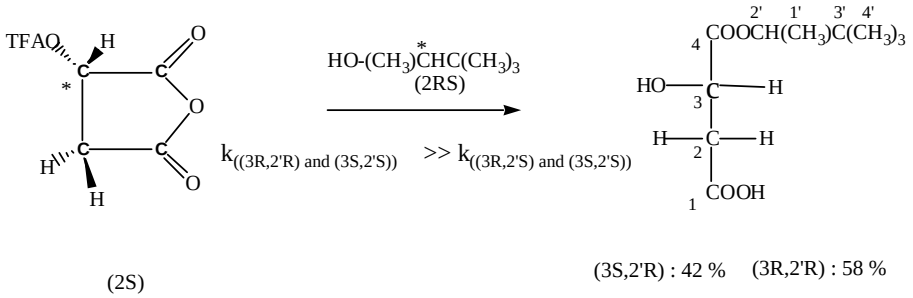
In conclusion of this part, chiral GC and ^{13}C NMR are successful tools for analyzing the different stereoisomers of the lactones and the configurational structure of the derivated polymers. These results are important in regard to the relationships structure/properties.

3.2. Thermal properties

With the aim to constitute a poly(malic acid) derivatives library, from where it will be possible to choose the best candidates for a given application, it was essential to compare the different polystereoisomers according their thermal properties (Table 4).

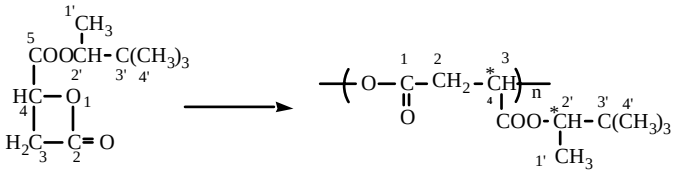
Racemic polymer **P1** (3*RS*,2′*RS*) is amorphous, contrary to both polydiastereoisomers **P1** (3*S*,2′*R*) and **P1**(3*S*,2′*S*). There is a small difference between both melting temperatures (about 10°C) due to two different configurational structures in the lateral chain. This observation is also verified for the glass transition temperature of three polymers which varies between 10°C and 40°C.

If we consider **P2**, the role of the pendant group in the thermal characteristics is increasing. At first, in this series, the racemic polymer presents a high melting temperature (180°C). This behaviour is uncommon and can be explained by the specificity of the bulky 3,3-dimethyl-2-butyl group and by the unbalance between couples of diastereoisomers [(3*R*,2′*S*) + (3*S*,2′*R*)] and [(3*R*,2′*R*) + (3*S*,2′*S*)], as noted above. Both chiral centers play a role in the organization



Scheme 2.

Table 3
Characteristics of 3,3-dimethyl-2-butyl malolactonates **2** and poly(3,3-dimethyl-2-butyl malolactonates) **P2**



2 **P2**

Lactone: expected configuration	% ((*R*,*S*) + (*S*,*R*))[a]	% ((*R*,*R*) + (*S*,*S*))[a]	Polymer	M_n[b]	Ip
(4*RS*,2′*RS*)	67	33	(3*RS*,2′*RS*)	38 000	1.6
(4*R*,2′*RS*)	59	41	[c]	–	–
(4*R*,2′*S*)	100	0	[c]	–	–
(4*S*,2′*S*)	0	100	[c]	–	–

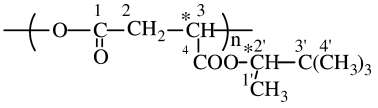
[a] Diastereoisomers % determinated by ^{1}H NMR.
[b] Calculated $M_n = 200\,000$.
[c] Insoluble in all solvents.

of the polymers. Indeed, the presence of the stereogenic center in the skeleton is important as shown by the difference between **P2**(3*S*,2′*S*) ($T_m = 268$°C) and **P2** (3*R*,2′*S*) ($T_m = 232$°C). It is also worth to note the high value of glass transition temperature (>100°C) for the optically active polymers.

3.3. Development of a semi-crystalline polyester family with controlled architecture, using malic acid and its alkyl derivatives as useful basic repeating units

Table 5 displays the behaviour of the semi-crystalline poly(benzyl 3-alkylmalates) and poly(alkyl and benzyl malates) previously investigated.

The presence of alkyl groups in the main chain increases largely the melting temperature in the case of poly(benzyl (3S,4S)-3-methylmalate)) ($T_m = 250$°C) compared to poly(benzyl (*S*)-malate) (180°C). It is worth to noting the importance of the configurational structure. The erythro form (3*R*,4*S*) of the repeating unit disturbs the stacking of the macromolecular chain in spherulites compared to the threo (3*S*,4*S*) form as displayed by the lower melting temperature (120°C) of poly(benzyl (3*R*,4*S*)-3-methylmalate). Moreover, the melting temperature can be directly correlated to the steric hindrance of the alkyl group as



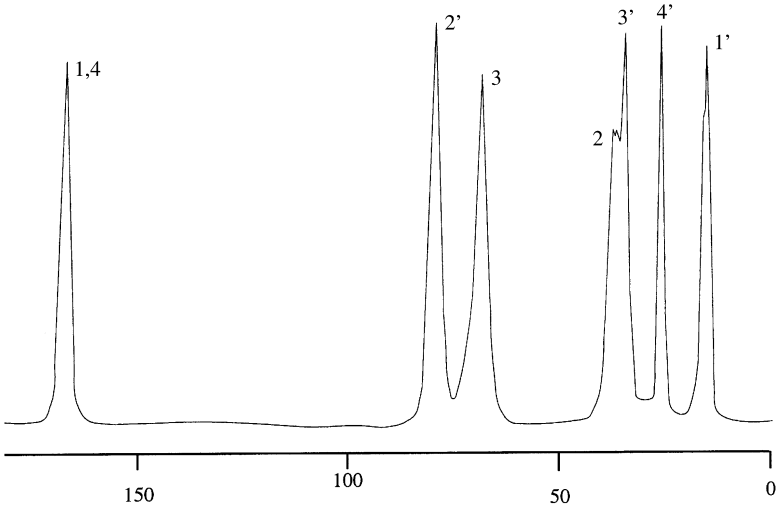


Fig. 3. **P2** (3*RS*,2′*RS*) solid state ^{13}C NMR spectrum.

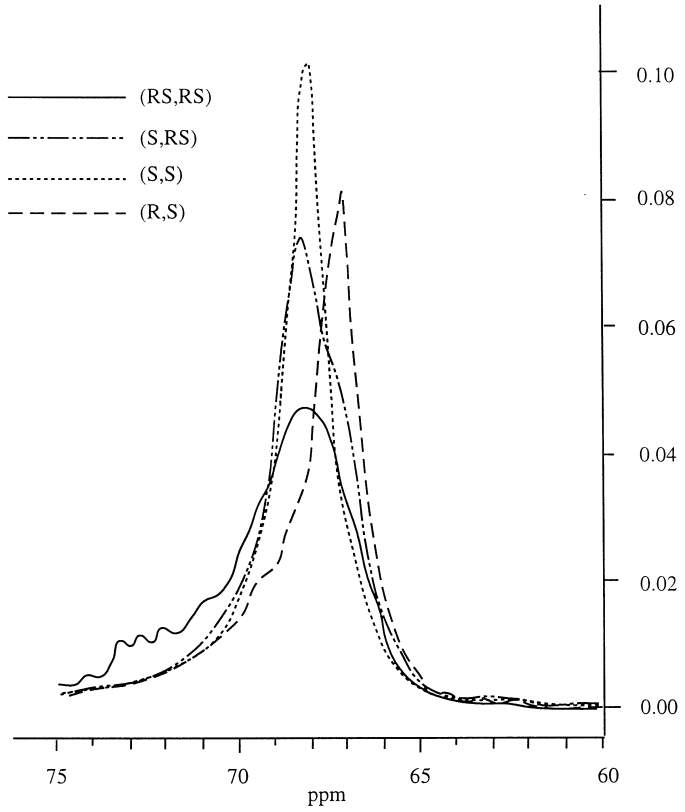


Fig. 4. 3C carbon atom ^{13}C NMR signals of **P2**.

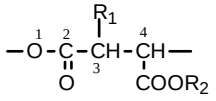
Table 4
Thermal characteristics of poly(2-butyl malates) **P1** and poly(3,3-dimethyl-2-butyl malates) **P2**

Polymer	T_g (°C)	T_m (°C)
P1 (3*RS*,2′*RS*)	10	–
P1 (3*S*,2′*R*)	40	170
P1 (3*S*,2′*S*)	35	160
P2 (3*RS*,2′*RS*)	36	180
P2 (3*S*,2′*RS*)	116	246
P2 (3*S*,2′*S*)	148	268
P2 (3*R*,2′*S*)	143	232

displayed by poly(benzyl (3*S*,4*S*)-3-ethylmalate) ($T_m = 200$°C) and poly(benzyl (3*S*,4*S*)-3-isopropylmalate) ($T_m = 176$°C). At last, it is possible to adjust the melting temperature by combining both diastereoismers repeating units. A stereocopolymer containing (3*R*,4*S*)/(3*S*,4*S*) stereoisomers of 3-methylmalic in a 80/20 mol/mol ratio presents a low melting temperature (40°C) and a good solubility in organic solvents.

If we compare polymers with the second stereogenic center in the lateral ester group, we observe low melting temperature and low glass transition temperatures when

Table 5
Comparison between thermal characteristic of different poly(malic acid esters)



Polymer	$R_2 = {}^{1'}CH_2{}^{2'}CH(CH)_3C_2H_5$				
$R_1 = H$	(4*RS*,2′*RS*)	(4*S*,2′*RS*)		(4*S*,2′*S*)	(4*S*,2′*R*)
T_g (°C)	−2	−5		−2	−5
T_m (°C)	–	60		80	84
Polymer	$R_1 = H$	$R_1 = CH_3$		R_1:C_2H_5	$R_1 = CH(CH_3)_2$
$R_2 = CH_2C_6H_5$	(4*S* or *R*)	(3*S*,4*S*)	(3*R*,4*S*)	(3*S*,4*S*)	(3*S*,4*S*)
T_g (°C)	37	–	55	–	–
T_m (°C)	180	250	120	200	176

the chiral center is in β position from carboxyl group; the pendant group plays the role of plasticizer. It is clear, from Tables 3 and 4, the increasing of both characteristic temperatures is important in the case of particular secondary alcohols as precursor of the ester pendant group.

4. Conclusion

In conclusion, the family of poly(malic acid) derivatives, which was developed at first as hydrolyzable polymers aimed at temporary applications, can be considered as a good candidate for taylor-made highly organized macromolecules structures in molecular imprinting recognition, enantioselective catalysis and high temperature stable polymeric systems. The mastery of the chemical and chemioenzymatic synthesis of functionalized β-substituted β-lactones open the route to a large library, which can be completed according to the required thermal characteristics. Versatility and potentiality of this polyesters family can be compared to the wide acrylic and methacrylic polymers library.

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