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# Synthesis and characterization of new polyesters based on renewable resources

Sandrine Waig Fang<sup>a,b</sup>, Pascale De Caro<sup>a,b</sup>, Pierre-Yves Pennarun<sup>c</sup>, Carlos Vaca-Garcia<sup>a,b</sup>,  
Sophie Thiebaud-Roux<sup>a,b,\*</sup>

<sup>a</sup> Université de Toulouse, INP, LCA (Laboratoire de Chimie Agro-Industrielle), 4 allée Emile Monso, F 31432 Toulouse, France

<sup>b</sup> UMR 1010 INRA/INP-ENSIACET, Toulouse, France

<sup>c</sup> 915, Route de Moundas, FR-31600 Lamasquère, France

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## ABSTRACT

A series of non-crosslinked biobased polyesters were prepared from pentaerythritol and aliphatic dicarboxylic acids, including fatty acids grafted as side-chains to the backbone of the polymer. The strategy utilized tends to create linear polymers by protecting two of the hydroxyl groups in pentaerythritol by esterification with fatty acids before the polymerization reaction. The solvent-free syntheses were performed under vacuum and catalyzed by the ion-exchange resin Amberlyst 70. The maximum yield was around 98%. Pristine polyesters had average molecular weights of about 10<sup>4</sup> g/mol according to SEC-MALLS analysis. Melting temperatures and extent of crystallinity were determined by differential scanning calorimetry. By using relatively short fatty acids, such as lauric acid, soft materials were obtained with low crystallinity and a melting point below room temperature, whereas longer side-chains, such as behenic acid, gave brittle polymers with higher melting temperatures and crystallinity. The use of a short chain dicarboxylic acid, such as succinic acid, resulted in closer side-chains and promoted higher crystallinity and melting temperatures. In order to improve the thermal properties of these materials, a series of copolyesters were designed by developing synthetic methods to approach a random- and a block-copolymerization. A wide range of properties was thus obtained according to the composition of these novel copolyesters.

## 1. Introduction

In the general context related to the dwindling of fossil resources, it is urgent to find new materials based on biomass and renewable resources to replace petroleum-based counterparts. A large number of monomers and polymers are available for a more sustainable chemistry, including poly(lactic acid), lignins, furan derivatives, sugars (Belgacem and Gandini, 2008; Gandini, 2011), and fatty acids derivatives (Montero de Espinosa and Meier, 2011; Xia and Larock, 2010; Meier et al., 2007). Some polyesters based on sucrose fatty acid esters or ricinoleic acid–lactic acid copolyesters are being developed as mild and non-toxic emulsifiers for food, cosmetics and pharmaceuticals (Akoh, 2002; Slivniak et al., 2006). Other biodegradable polyesters, based on glycerol, sorbitol or pentaerythritol have been widely studied for their adhesive properties (Kricheldorf and Behnken, 2008) or for medical applications (Kline et al., 1998; Kumar et al., 2003) or for their good water solubility (Zhao et al., 2009). Given the multifunctional nature of such polyols

(glycerol or pentaerythritol), the preparation of homogeneous non-crosslinked polyesters by polycondensation using diesters or dicarboxylic acids as monomers is a complex task because their numerous hydroxyl groups result in the creation of networks (Kricheldorf and Behnken, 2008; Murillo et al., 2009; de Meireles Brioude et al., 2007). Therefore, such syntheses may require a multistep reaction pathway including protection and deprotection of monomer units. In this context, some researchers reported a simple strategy to prepare aliphatic poly(butylene succinate-co-butylene maleate) and polybutylene tartrate (Zhang et al., 2003; Hao et al., 2005). Shibata and Takasu (2009) proposed a one-step bulk synthesis of polyesters with pendent hydroxyl groups under mild conditions using rare-earth catalysts. Other chemical routes to produce polyester by condensation polymerization were developed from vegetable oils derivatives: ring-opening polymerization of lactones, polycondensation between a diacid (or diester) and a diol (or monoglycerides) or polycondensation of hydroxy-acids or esters (Xia and Larock, 2010; Bakare et al., 2006). For example, high molecular weight linear polyesters can be obtained by three steps: ozonolysis and reduction of castor oil followed by methanolysis and then, transesterification of the obtained hydroxy methyl ester for polymerization (Petrovic et al., 2010).

In recent years, enzyme-catalyzed syntheses have emerged as interesting green alternatives (Meier et al., 2007; Kelly and Hayes,

\* Corresponding author at: UMR 1010 INRA/INPT-ENSIACET, Laboratoire de Chimie Agro-industrielle, 4 allée Emile Monso, BP 44362, 31030 Toulouse cedex 4, France. Tel.: +33 5 34 32 35 04; fax: +33 5 34 32 35 97.

E-mail address: [sophie.thiebaudroux@ensiacet.fr](mailto:sophie.thiebaudroux@ensiacet.fr) (S. Thiebaud-Roux).

2006; Uyama and Kobayashi, 2006), allowing to limit branching and obstruct cross-linking reactions (Yang et al., 2011). Thus, immobilized lipases (Novozyme 435) were used for a one pot synthesis to prepare both linear and hyperbranched copolymers containing glycerol (Kulshrestha et al., 2005). In the presence of toluene, lipase-catalyzed polycondensation of unsaturated dicarboxylic acids with diols led to polyesters containing carbon-carbon double bonds (Yang et al., 2010). In similar conditions, the polymerization of bio-based diols and di-carboxylic acids via cyclic oligomers was performed by Yagihara and Matsumura (2012). However, these syntheses were carried out under a reduced pressure or nitrogen atmosphere and required very long reaction times (between 42 and 48 h), as the temperature should not exceed 60 °C to preserve the activity and the stability of lipases. Therefore, Korupp et al. (2010) have mentioned that the mechanical stability of enzyme towards energy input brought by the mixture might be a major problem for a scale-up.

To synthesize biobased polyesters according to a green approach, we have considered esterification methods using heterogeneous catalysis through ion-exchange resins (Park et al., 2010; Pouilloux et al., 1999). Thus, Pouilloux et al. (1999) esterified oleic acid with glycerol at 90 °C with different Amberlyst resins that can be readily removed from the final product. Amberlyst 31 gave the highest yield (50%) and the selectivity to monooleyl glyceride was over 90%. Under some conditions, ion-exchange resins suffer from poor thermal stability, which restricts their use to 150 °C and a relatively low acid strength. Amberlyst 70 shows a higher thermal stability compared with that of other resins, and a high resistance to desulfonation, even at 190 °C (Siril et al., 2007).

The purpose of this work was to synthesize polyesters using pentaerythritol, a dicarboxylic acid and different length fatty acids as pendant chains to obtain selectively bifunctional compounds and to promote the synthesis of linear polymers. Solvent-free synthesis of the polyesters was carried out in order to obtain either statistical or block co-polyesters in two or three steps. In order to limit crosslinking, esterification was first conducted between fatty acids and polyalcohol to produce expected bifunctional monomers (depending of the ratio of alcohol and acid functions). The obtained polyol fatty acid esters were then used as monomers in a second step to be polymerized with dicarboxylic acids. An experiment design was applied to reach the optimum yield and selectivity. Then, the influence of the nature of the fatty acid in the side-chains and of the dicarboxylic acid in the polymer backbone on the thermal properties of the ensuing polyesters was studied.

## 2. Materials and methods

### 2.1. Materials

Pentaerythritol (POH), glycerol (GOH) and lauric acid (AL, C12:0) were purchased from Sigma Aldrich, stearic acid (AS, C18:0) and adipic acid (AD, HOOC(CH<sub>2</sub>)<sub>4</sub>COOH) from Acros, sebacic acid (ASeba, HOOC(CH<sub>2</sub>)<sub>8</sub>COOH) from Merck and succinic acid (ASuc, HOOC(CH<sub>2</sub>)<sub>2</sub>COOH) from Carlo Erba. All chemicals were obtained in the highest purity available. Technical grade (purity over 80%) triglycerol (TriGOH) and behenic acid (AB, C22:0) were purchased from Sigma Aldrich. All monomers were used without any further purification. Amberlyst 70 was kindly provided in the form of wet beads by Rohm and Haas. Prior to any esterification, the resin was washed and dried under vacuum at 40 °C for 24 h.

### 2.2. Measurements

FTIR spectra were obtained with KBr disks using a JASCO FTIR-460 plus spectrometer. The <sup>1</sup>H NMR spectra were performed on a

Bruker Advance 300 MHz spectrometer. The molecular weights of the polyesters were measured by size exclusion chromatography-multiangle light scattering (SEC-MALLS) using a Dionex HPLC system equipped with a PS80 pump, an ASI 100 autosampler, a Crocicol oven, a Iota-2 refractometer and a multiangle laser light scattering photometer Wyatt-miniDawn TREOS. A three-column set PLgel 5 μm, from Polymer Laboratories, of pore size 1000 Å, 500 Å and 100 Å in series, was used to analyze the samples. A polystyrene standard (Polymer Laboratories) with a molecular weight of 30,000 g/mol were used to calibrate the Wyatt minidawn TREOS. The relative molecular weight of the pre-polymers were measured using polyethylene glycol standards (Polymer Laboratories) with molecular weight range from 600 g/mol to 20,000 g/mol to calibrate the refractometer. Tetrahydrofuran (THF), at 30 °C, with a flow rate of 0.8 mL min<sup>-1</sup> was used as eluent. The specific refractive index increments (*dn/dc*) in THF at 30 °C were measured with a Dndc 2010 PSS refractometer at 620 nm. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer Pyris 1. In order to provide the same thermal history, each sample was preheated from room temperature to 100 °C at a heating rate of 10 °C min<sup>-1</sup> then cooled down to -40 °C at the same rate. The DSC scan was then recorded by heating from -40 °C to 150 °C at 4 °C min<sup>-1</sup> in a nitrogen atmosphere. The cation exchange capacity of the dried resin (2.34 mmol g<sup>-1</sup>) was determined by percolating an aqueous NaCl solution, followed by titration with a 0.1 N NaOH solution.

### 2.3. Preparation of polymers

All polymers were prepared by bulk polymerization, catalyzed with the ion exchange resin Amberlyst 70 (0.05 eq H<sup>+</sup>/mol pentaerythritol). In order to prevent crosslinking or gelation, synthesis were conducted in two or three steps. The two-steps reaction led to random copolymers, whereas the three-steps process tends to yield block-like configuration.

To produce random copolymers, fatty acids were esterified with pentaerythritol to give the corresponding esters. In order to enhance the miscibility of pentaerythritol in the fatty acid, a small amount of triglycerol (10 mol% compared to pentaerythritol) or glycerol (33 mol%) had to be added. In a typical formulation, a mixture of pentaerythritol (1 g, 7.35 mmol), triglycerol (0.176 g, 0.74 mmol), stearic acid (3.07 g, 10.80 mmol), lauric acid (0.24 g, 1.20 mmol) and 0.17 g of Amberlyst 70 was introduced in a cylindrical glass reactor equipped with a magnetic stirrer, gas-inlet and gas-outlet tubes. The system was heated at 160 °C and atmospheric pressure for 1 h and at reduced pressure (40 mbar) for one more hour. It was then heated to 180 °C and the pressure lowered to 20 mbar for 4 more hours. After 30 min under these conditions, the mixture became a clear monophasic liquid. In the second step, a dicarboxylic acid was added in stoichiometric conditions and polymerization occurred. For example, 1.18 g (8.09 mmol) of adipic acid was added and the bulk polymerization continued for 5 h. The ensuing product was cooled to approximately 60 °C and filtered to remove the resin. The light-yellow random copolymer was homogeneous and showed no gel particles.

To prepare block-copolyesters containing long fatty acids in one block (i.e. behenic and stearic acid) and short fatty acids (i.e. lauric acid) in the other block, we proceeded in three steps. The first step was identical to the synthesis of random copolyesters and provided blends of pentaerythritol (and glycerol, or triglycerol) fatty acid esters; some blocks are obtained from lauric acid and others from a mixture of stearic and behenic acids. Then, 60% of the total amount of dicarboxylic acid was first added and the remaining quantity after 4 h of pre-polymerization. This last step of polymerization was carried out for 3.5 h. The ensuing product was filtered and the copolymer was analyzed without further purification.

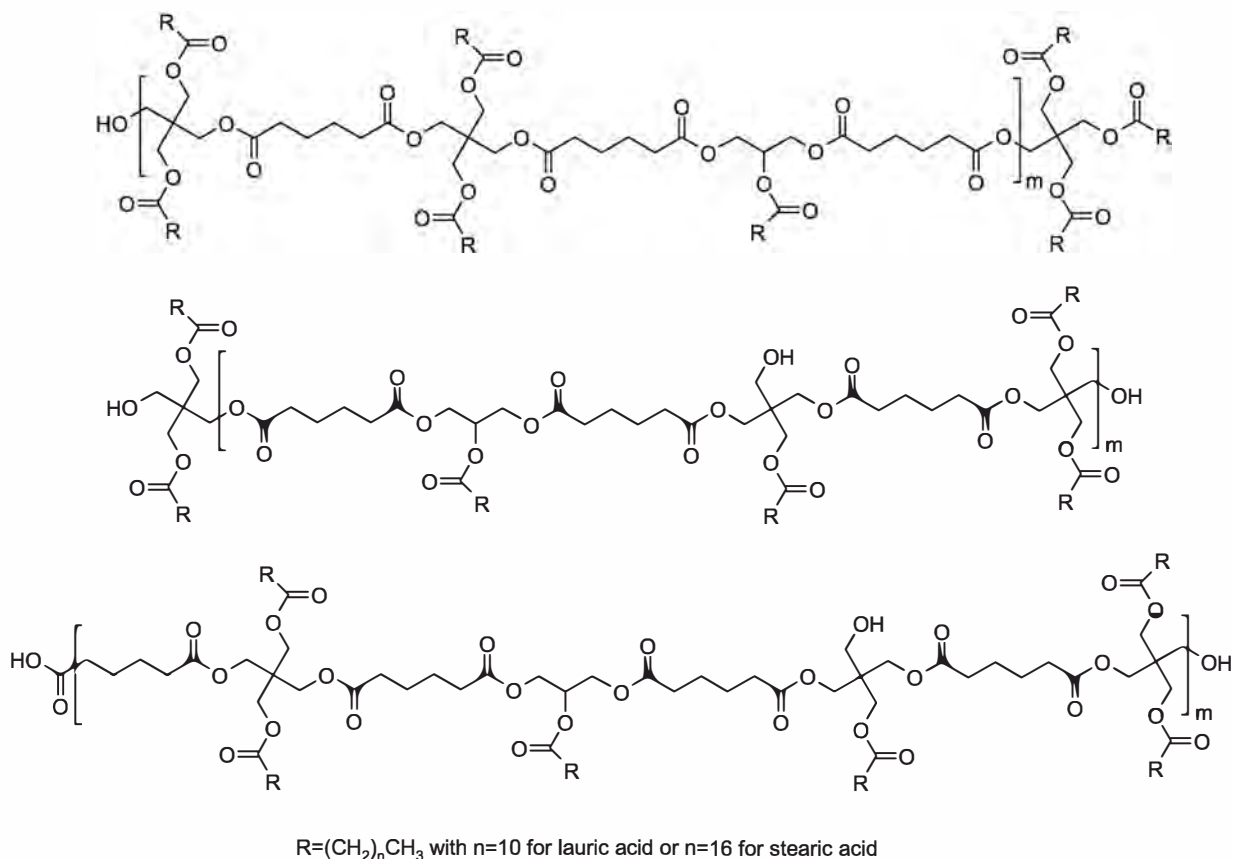


Fig. 1. Examples of target ideal structures of random copolymers from pentaerythritol, glycerol, fatty acids (lauric or stearic acids) and adipic acid.

### 3. Results and discussion

The synthetic strategy used to prepare the polyesters as much linear as possible by polycondensation from dicarboxylic acids and pentaerythritol is the protection by esterification with fatty acids of some hydroxyl groups in pentaerythritol before the polymerization reaction itself. Due to the insolubility of pentaerythritol in the fatty acid medium, the former was mixed with glycerol or triglycerol. The branched statistical or block co-polyesters targeted are represented in Figs. 1 and 2. They were produced by polycondensation between diacids (such as adipic acid) and fatty acid esters of pentaerythritol and (glycerol or triglycerol), which were firstly synthesized by polyol esterification (Fig. 3).

#### 3.1. Analysis of the first step product

The first step of esterification using fatty acids and polyalcohols as starting materials led to a mixture of mono-, di-, and tri-substituted alcohols assessed by SEC. The tetra-derivatives

appeared in very low concentration. The highest contents of di-substituted alcohols were expected to favor linear polyester in the next step of the polymerization. These compositions were assessed by SEC. Fig. 4 shows the SEC chromatograms of blends arising from several experiments involving a molar ratio pentaerythritol:glycerol of 1:0.33 and variable amounts of stearic acid, according to reaction time. With this experimental design, we estimated by SEC that the highest yield (94%) and selectivity (around 40% of di-substituted alcohol) were obtained with a fatty acid/polyol molar ratio of 1.45 and a reaction time of 5.25 h, as summarized in Table 1. These conditions were then applied to all the other syntheses discussed here.

In order to compare the influence of the fatty acid, pentaerythritol laurate esters, pentaerythritol stearate esters and pentaerythritol behenate esters were synthesized. Fig. 5 shows the  $^1H$  NMR spectrum of the behenic acid esterified by pentaerythritol and triglycerol (10:1 mol). The chemical shifts of the protons of the  $CH_2$  groups in  $\alpha$ -positions of ester or alcohol functions are different for mono, di and tri-substituted pentaerythritols. Therefore,

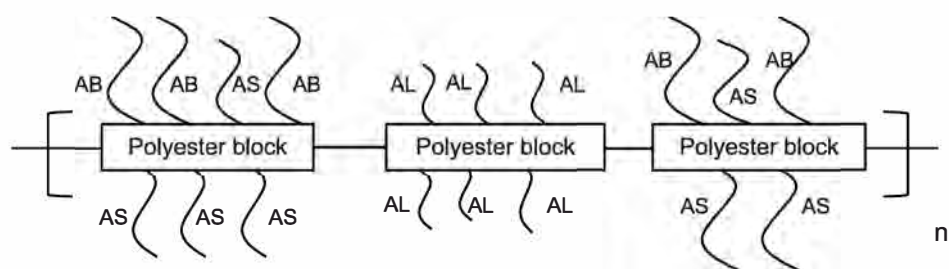
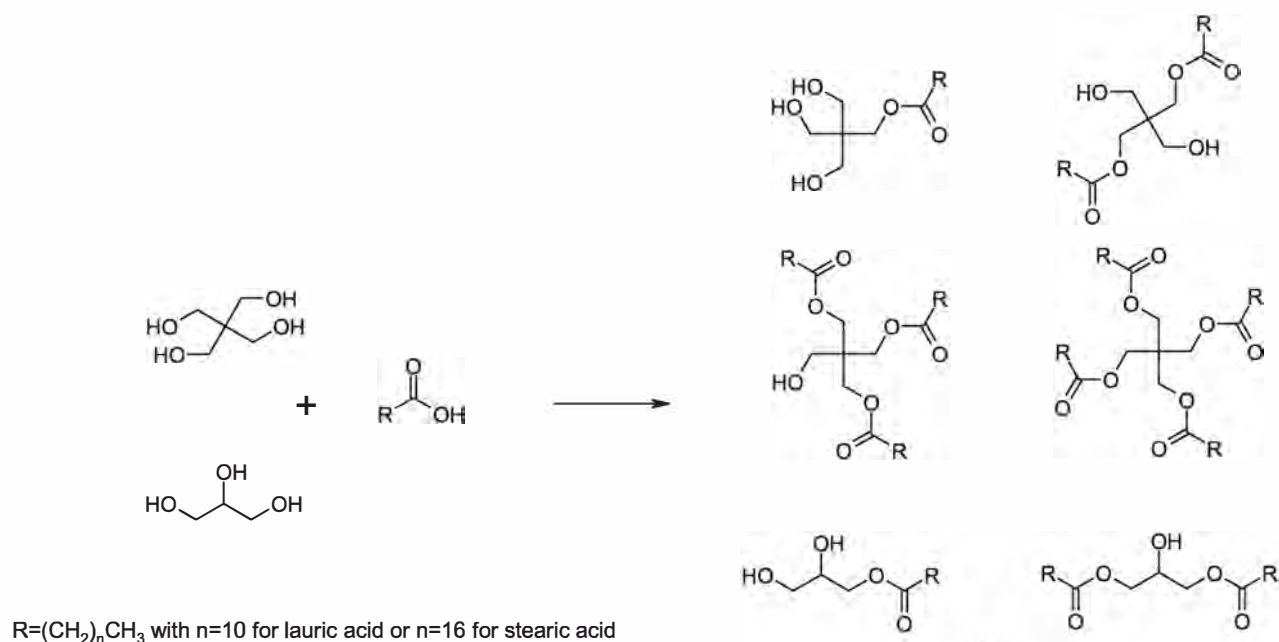
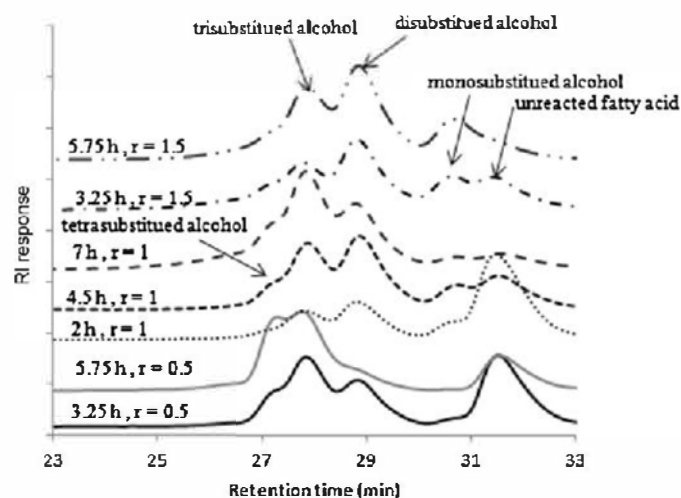


Fig. 2. Example of a block-copolymer (with AL lauric, AS stearic or AB behenic esters as side-chains).



**Fig. 3.** Mono- and polysubstituted polyols (pentaerythritol and glycerol based fatty acid esters) likely to be obtained at the first reaction step.

the proportions of mono-, di- and tri-substituted alcohols could be calculated by either <sup>1</sup>H NMR or SEC. For the chromatographic analyses, we considered that the response factors are similar for the mono-, di- and tri-substituted pentaerythritols, which can explain the slightly different results compared to those obtained by <sup>1</sup>H NMR (Table 2). The NMR yield was the lowest for pentaerythritol monolaurate, which means that lauric acid reacted faster than the longer fatty acids. These results are explained by lower steric hindrance and viscosity of C12 chains promoting their reactivity. Tetra-substituted pentaerythritols were found in very small amounts, obviously because of steric hindrance. Tri-substituted pentaerythritol may constitute dead chain ends when they react with the dicarboxylic acid in the second step. The mono-substituted



**Fig. 4.** Size exclusion chromatograms of the polyesters from stearic acid obtained with a molar ratio pentaerythritol:glycerol = 1:0.33. (r = molar ratio fatty acid/polyol).

**Table 1**

Results of the design of experiments from stearic acid and a mixture of pentaerythritol and glycerol [1:0.33] (mol).

Run	AS:polyol	Time (h)	Yield <sup>a</sup> %	Selectivity <sup>b</sup> %
1	0.5	3.25	75.7	22.7
2	0.5	5.75	82.8	12.1
3	1	2	80.7	22.5
4	1	4.5	92.1	37.8
5	1	7	95.7	31
6	1.5	3.25	92.2	38.2
7	1.5	5.75	96.2	39.5
8	1.4	5.8	96.2	39.7
9	1.45	5.25	94.0	40.6

<sup>a</sup> Yield = [1 - (area of the residual monomer/total area)] × 100 (areas were measured by SEC analysis).

<sup>b</sup> Selectivity = [area of bifunctional alcohol/total area] × 100 (areas were measured by SEC analysis after the esterification of fatty acid with alcohol).

pentaerythritol may cause branching on the polymer backbone and even cause cross-linking between the polymer chains. Therefore, equimolar ratio polyol/dicarboxylic acid was used for the polymerization step in order to prevent the polyol tri-substitution and the gelation as described by Kricheldorf and Behnken (2008) for the polycondensation of pentaerythritol and dimethyl sebacate.

**Table 2**

Percentages of mono-, di- and tri-substituted alcohols determined by <sup>1</sup>H NMR and SEC analyses under the following conditions: molar ratios pentaerythritol:triglycerol = [10:1], fatty acid:polyol = [1.45:1] with lauric, stearic or behenic acid as fatty acid.

	Lauric acid		Stearic acid		Behenic acid	
	SEC	<sup>1</sup> H NMR	SEC	<sup>1</sup> H NMR	SEC	<sup>1</sup> H NMR
% mono-substituted	31	28	20	30	29	33
% di-substituted	39	45	33	45	34	39
% tri-substituted	29	27	46	25	36	28

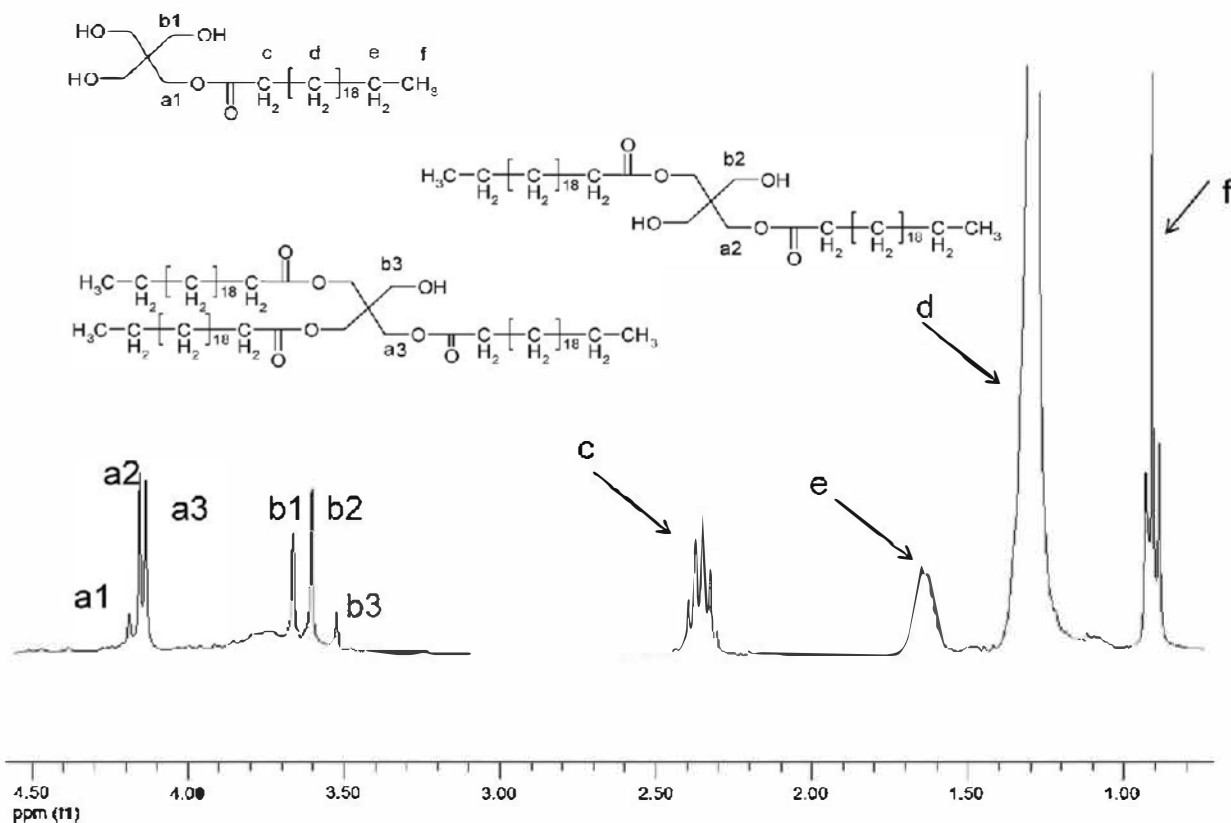


Fig. 5.  $^1\text{H}$  NMR spectrum of the compound resulting from the esterification of behenic acid with a mixture of pentaerythritol and triglycerol [10:1] (mol) in  $\text{CDCl}_3$ .

### 3.2. Characteristics of the random copolymer

After esterification of the fatty acid by pentaerythritol and glycerol (or triglycerol), polymers and copolymers were synthesized by the addition of the dicarboxylic acid such as adipic acid ( $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ ), succinic acid ( $\text{HOOC}(\text{CH}_2)_2\text{COOH}$ ) or sebacic acid ( $\text{HOOC}(\text{CH}_2)_8\text{COOH}$ ).

#### 3.2.1. Influence of the fatty acid

Table 3 gives the results of experiments based on the polycondensation of the polyol fatty acid esters and diacids. The average content of unreacted hydroxyl groups was measured by  $^1\text{H}$  NMR and ranged between 9 and 13%. This result was confirmed by FTIR spectroscopy: a peak around  $3400\text{ cm}^{-1}$  corresponds to the stretching vibrations of hydroxyl groups and the other characteristic signals of polyesters were found at  $1731\text{ cm}^{-1}$  for the stretching vibrations of  $\text{C}=\text{O}$  bonds and at  $1150\text{--}1050\text{ cm}^{-1}$  for  $\text{C}-\text{O}-\text{C}$  linkages. Pentaerythritol grafted with long side-chains, like those from behenic acid, were less reactive than pentaerythritol grafted with lauric acid, anticipating a lower yield for the behenic-based polymer. This was indeed confirmed by the results (Table 3, entry 1 to 3), which indicated that when the length of the hydrocarbon side-chain increased, both reaction yield and average molecular weight decreased.

Concerning the thermal properties, polymers with long side-chains showed higher melting enthalpy and melting temperature. No glass transition temperature was observed for these polyesters. For the copolymers, increasing the amount of long fatty acids (i.e. behenic or stearic acid) enhanced the melting temperature and the crystallinity. In Table 3, polymer 9, with the lowest stearic acid content ( $[\text{AS}:\text{AL}] = [6:4]$  mol), showed lower melting temperature ( $27^\circ\text{C}$ ), compared with those of polymers 7 and 8. When

behenic acid ( $\text{C}_{22:0}$ ) (5% molar compared to the total amount of fatty acids) was added, the melting temperature rose from  $28^\circ\text{C}$  to  $30^\circ\text{C}$  (Table 3, polymers 10, 11). When behenic acid completely replaced stearic acid in the formulation, the melting temperature increased to  $50^\circ\text{C}$  (Table 3, entry 12). The obtained melting temperatures are most likely due to side-chain crystallization if these branched chains are long enough. This phenomenon was shown to depend on the degree of chain branching and the branch length (Watanabe et al., 1994; Jin et al., 2000; McKee et al., 2005). Above a given branch length depending of the polyester, the melting temperature tends to increase, due to ordering and crystallization of the side-chains. Crystals can also incorporate overlapping or interdigitated side-chains from neighboring main chains. It has been demonstrated in other type of polymers, especially in cellulose derivatives with fatty chains longer than octanoic (Sealey et al., 1996). The global consequence is an increase of crystallinity and a higher melting temperature.

#### 3.2.2. Influence of the dicarboxylic acid

In the backbone of the polymer, sebacic acid, adipic acid and succinic acid as dicarboxylic acids were used. The increase of the hydrocarbon chain length resulted in a lower melting temperature. The melting temperature was  $31^\circ\text{C}$  for succinic acid,  $28^\circ\text{C}$  for adipic acid and reached  $21^\circ\text{C}$  for sebacic acid (Table 3, entries 14, 10 and 13). Fig. 6 shows the DSC curves of the three polymers. The main peaks reflect the melting temperature of the polymers, while secondary peaks were attributed to fraction of oligomers or tri- and tetra-substituted pentaerythritols. Once again, crystallization of the side-chains is involved. A shorter dicarboxylic acid makes the side-chains closer, and thus crystallinity increases. As expected, polymers built with succinic acid were brittle, whereas sebacic acid based counterparts were soft.

**Table 3**

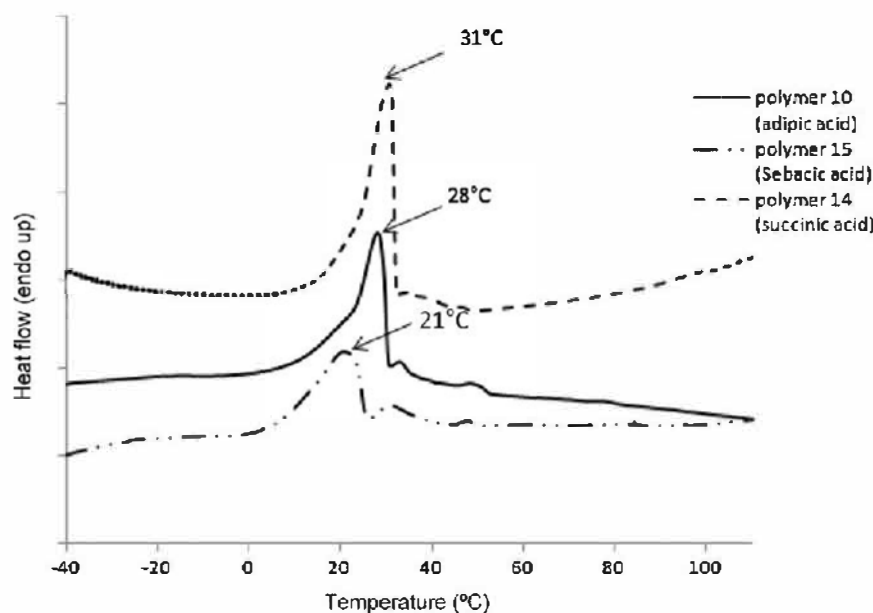
Composition and characterization of random copolyesters: average  $M_n$  and  $M_w$  measured by SEC-MALLS analysis, melting temperature and melting enthalpy, measured by DSC analysis.

Run	Polyols <sup>a</sup>	Fatty acid <sup>b</sup>	Dicarboxylic acid <sup>c</sup>	Yield %	$M_n$ (g/mol)	$M_w$ (g/mol)	$T_m$ (°C)	$\Delta H$ (J/g)
1	POH:TriGOH [10:1]	AB	AD	89	$3.84 \times 10^3$	$7.46 \times 10^3$	63	129
2	POH:TriGOH [10:1]	AS	AD	90	$2.28 \times 10^5$	$2.85 \times 10^6$	41	79
3	POH:TriGOH [10:1]	AL	AD	96	$3.77 \times 10^4$	$1.48 \times 10^5$	25	51
4	POH:TriGOH [10:1]	AS:AL [9:1]	AD	92	$1.41 \times 10^4$	$2.02 \times 10^5$	41	77
5	POH:TriGOH [10:1]	AS:AL [7:3]	AD	90	$1.47 \times 10^4$	$1.01 \times 10^5$	37	57
6	POH:TriGOH [10:1]	AB:AS:AL [0.5:6:3.5]	AD	89	$3.39 \times 10^4$	$1.96 \times 10^5$	32	36
7	POH:GOH [10:3]	AS:AL [9:1]	AD	95	$3.35 \times 10^4$	$1.71 \times 10^5$	36	60
8	POH:GOH [10:3]	AS:AL [7:3]	AD	94	$1.40 \times 10^4$	$1.01 \times 10^5$	31	47
9	POH:GOH [10:3]	AS:AL [6:4]	AD	96	$1.67 \times 10^4$	$6.68 \times 10^4$	27	44
10	POH:GOH [10:3]	AS:AL [6.5:3.5]	AD	98	$1.61 \times 10^4$	$6.66 \times 10^4$	28	54
11	POH:GOH [10:3]	AB:AS:AL [0.5:6:3.5]	AD	90	$1.78 \times 10^4$	$1.03 \times 10^5$	30	52
12	POH:GOH [10:3]	AB:AL [6.5:3.5]	AD	89	$1.62 \times 10^4$	$1.19 \times 10^5$	50	124
13	POH:GOH [10:3]	AS:AL [6.5:3.5]	Aseba	94	$9.37 \times 10^3$	$2.43 \times 10^4$	21	43
14	POH:GOH [10:3]	AS:AL [6.5:3.5]	Asuc	93	$1.3 \times 10^4$	$4.6 \times 10^4$	31	40
15	POH:GOH [10:3]	AS:AL [7:3]	Aseba	92	$2.92 \times 10^3$	$8.62 \times 10^3$	23	51

<sup>a</sup> POH: pentaerythritol; GOH: glycerol; TriGOH: triglycerol.

<sup>b</sup> AL: lauric acid; AS: stearic acid; AB: behenic acid (molar ratio fatty acid:polyol = 1.45:1).

<sup>c</sup> AD: adipic acid; Aseba: sebacic acid; Asuc: succinic acid (molar ratio dicarboxylic acid:polyol = 1:1).



**Fig. 6.** DSC thermograms of random copolyesters based on succinic acid, adipic and sebacic acid (obtained under the experimental conditions given in Table 3, for Run 14, 10 and 13).

### 3.3. Characteristics of the block copolyesters

The block copolyesters were prepared by copolymerization of two blocks synthesized separately with one of the three diacids. Each block was obtained in a previous step by pre-polymerization of the same dicarboxylic acid and one kind of pentaerythritol fatty acid esters (prepared from polyols mixture and lauric acid for the first block, or stearic acid, associated or not to behenic acid, for the second block). The results relative to the block copolyesters are summarized in Table 4.

Polymers of Table 3, entry 9, and Table 4 entry 16, shared the same monomers in the same proportions. Yet the block copolyester showed a melting temperature of 34 °C and that of the random one was only 27 °C. The random copolymer of Table 3, entry 6, showed a melting temperature of 32 °C, while that of the corresponding block copolymer of Table 4, entry 19, was 36 °C. When succinic acid was used in the backbone instead of adipic acid, the melting temperature increased from 33 °C to 39 °C (Table 4, entries 17 and 18). These results showed that the micro-crystallinity is higher in these block structures because of the intra- and inter-molecular stackings of

**Table 4**

Formulation and characterization of block copolyesters.

Run	Polyols	Fatty acid	Dicarboxylic acid	$M_n$ (g/mol)	$M_w$ (g/mol)	$T_m$ (°C)	$\Delta H$ (J/g)
16	POH:GOH [10:3]	AS:AL [6:4]	AD	$1.29 \times 10^4$	$2.58 \times 10^4$	34	52
17	POH:TriGOH [10:1]	AS:AL [6.5:3.5]	AD	$1.48 \times 10^4$	$4.41 \times 10^4$	33	50
18	POH:TriGOH [10:1]	AS:AL [6.5:3.5]	Asuc	$8.26 \times 10^4$	$1.01 \times 10^5$	39	61
19	POH:TriGOH [10:1]	AB:AS:AL [0.5:6:3.5]	AD	$3.91 \times 10^4$	$3.56 \times 10^4$	36	40

side-chains involved in these polymers. Thus, the synthesis of block copolyesters is a performing method to increase the melting point.

#### 4. Conclusion

In this study, we described the bulk synthesis of polyesters with fatty acid side-chains, using an ion exchange resin as catalyst. Amberlyst 70 allowed to obtain a maximum yield as high as 98% and was easy to remove from the final product. The copolyalcohol, i.e. glycerol or triglycerol, prevented the use of organic solvent and enabled a better contact between pentaerythritol and the fatty acids in a one-pot system with sequential addition of the reactants. We showed that longer side-chains increased the crystallinity and rose the melting temperature, due to side-chain crystallization. Shortening the length of dicarboxylic acid in the backbone produced an increase in both crystallinity and melting temperature. In all the cases, the block copolyesters showed higher melting temperature than the random ones.

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