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Bio-based polyricinoleate and polyhydroxystearate: properties and evaluation as viscosity modifiers for lubricants

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Abstract

This paper aims to design bio-based polyester as viscosity modifiers for lubricant properties. Bio-based polyricinoleate (PRic) and its saturated homologous polyhydroxystearate (PHS) have been synthesized from fatty acid methyl esters. The polycondensation performed in bulk in one-step reaction without any purification leads to two series of polyesters within a large range of molecular weights, with M_w between 3 and 130 kg.mol⁻¹. Their thermal properties were investigated. Good thermal stability was observed with degradation temperatures above 300 °C. As expected, PRic appeared to be amorphous with a particularly low glass transition temperature while PHS is semi-crystalline. A rheological study determined that polyricinoleate entangled when its molecular weight is above 25 kg.mol⁻¹. These two bio-based and biodegradable polymers were then evaluated as viscosity modifiers in both organic and mineral oils. PHS with high molecular

weights appeared to be an excellent thickener as well as a good Viscosity Index improver with a VI increase above +50 in organic lubricant oil and +64 in mineral oil.

Keywords: polyricinoleate, polyhydroxystearate, lubricant, viscosity modifiers, thickeners, Viscosity Index

Introduction

The global concern over environmental pollution has led to a growing interest in the use of renewable resources in the fields of polymers and lubricants. The abundant availability and relatively low cost of vegetable oils make them one of the most essential sustainable resources for the chemical industries.¹⁻³ Castor oil, in particular, represents a high interest for industrial applications; especially, ricinoleic acid can be recovered from castor oil triglycerides to its acidic form by saponification or to methyl ricinoleate by methanolysis.^{4,6} The natural presence of one OH group and a carboxylic or ester terminal function of this mono-unsaturated fatty acid/ester (C18:1, OH) enables its self-condensation to produce polyricinoleate which generally exhibit low molecular weights, i.e. 3-11 kg.mol⁻¹.⁵⁻¹² Only Matsumura and coll.^{13,14} synthesized amorphous polyricinoleate with M_w up to 100 kg.mol⁻¹ by mean of enzymatic catalysis. However, these systems require a large quantity of enzyme, 50 wt.% with respect to the monomer, very long reaction times and the use of solvents. More recently, our group reported the polymerization of methyl ricinoleate and its copolymerization with 12-hydroxystearate using Ti(OiPr)₄ as a catalyst leading to the formation of polyricinoleate with M_w up to 60 kg.mol⁻¹.¹⁵

This amorphous bio-based polyester appeared to be soluble in non-polar solvent and oils with thickening ability.¹⁰ Its high miscibility with apolar systems, its biodegradability feature and stability against temperature make polyricinoleate a promising environmental-friendly viscosity modifier for lubricants.^{7,10,13,16}

The role of a viscosity modifier is to thicken a lubricant oil and to reduce its viscosity loss at high temperature which is usually determined by the Viscosity Index (VI). Thanks to the addition of a viscosity modifier, a lubricant can be used over a large range of temperatures.^{17,18} Currently, mostly petroleum-based polymers such as polyalkylmethacrylates and polyolefins are used as viscosity modifiers.¹⁹⁻²¹ While the research is active on bio-compatible lubricants²²⁻²⁴, only a few solutions have been described to replace viscosity modifier additives with bio-based polymers in accordance to new environmental concerns.^{25,26}

Herein, polyricinoleate (PRic) was developed as well as its saturated homologous poly(12-hydroxystearate) (PHS) within a large range of molecular weights in order to evaluate these bio-based polyesters as potential viscosity modifiers. The molecular weights were controlled as a function of the reaction time. Both polyesters were synthesized using one-step bulk polycondensation, without further purification, and their thermal and rheological properties, in the bulk state, analyzed as a function of their molecular weight. Finally, the potential of PRic and PHS as viscosity modifiers in mineral and organic lubricant oils were evaluated.

Material and methods

Materials

Bio-based methyl ricinoleate (Nu-chek-prep, >99%) and methyl hydroxystearate (Nu-check-prep, >99%) were used without further purification for polyester synthesis. Titanium isopropoxyde (Ti(OiPr)₄, 99.99%, Acros Organics) was used as catalyst as received. Dichloromethane (DCM) was supplied from ABCR and used as received. Deuterated solvents were purchased from Eurisotop and used as received. Commercial mineral paraffinic oil, the Yubase 4+ (MO) and organic triglyceride oil, Radialube 7386 (OTO) were kindly supplied by TOTAL and Oleon, respectively. Their properties are given in Table 1. Two commercial viscosity modifiers were

kindly provided from Croda (Ref-O, specifically used in organic oil OTO) and from Chevron (Ref-M, specifically used in mineral oil).

Table 1: Oil characteristics, determined experimentally or from producer data sheet [in brackets]

Lubricant oils	MO	OTO
Density ¹	0.8226 [0.825]	0.941 [0.945]
Mn (g.mol ⁻¹) ²	600	750 [512.8]
D ²	1	1
Flash point (°C)	[220]	[235]
η at 40°C (mm ² .s ⁻¹) ¹	18.6	20.4
η at 100°C (mm ² .s ⁻¹) ¹	4.3 [4.1]	4.6 [4.5]
Viscosity Index VI	128	152

1- η= dynamic viscosity, 1 mm².s⁻¹ = 1 cSt; Obtained using a densimeter-viscosimeter at 40°C.

2-Obtained by SEC in THF, PS calibration, $D = M_w/M_n$, the dispersity.

Polyester synthesis

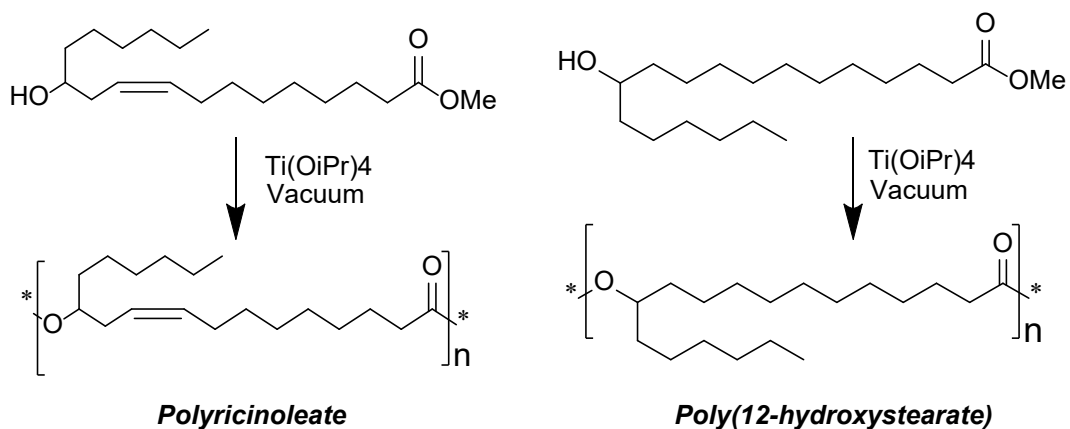


Figure 1: Synthesis of PRic and PHS

General procedure of polycondensation

PRic and PHS were prepared from methyl ester ricinoleate (1.5 g, 4.8 mmol) and methyl-12-hydroxystearate (1.5 g, 4.8 mmol), respectively (see Figure 1), dried overnight under vacuum at 70 °C under mechanical stirring in 50 mL Schlenk flask at 200 rpm. The mixture was cooled at room temperature under static vacuum and a 5 wt.% solution of Ti(OiPr)₄ in DCM (0.015 g of catalyst, 0.053 mmol, 1 wt.%) was added under nitrogen flow. The mixture was stirred at room temperature for 30 min under static nitrogen then put under vacuum and heated at 70 °C for 30 min. Then the mixture was heated at 120 °C for one hour, 140 °C for another hour and 180 °C for 45 hours still under dynamic vacuum to remove the methanol (MeOH) sub-product and mechanical stirring at 200 rpm. After 48 hours reaction, stirring was stopped, the highly viscous mixture was cooled to room temperature and the flask was opened to air in order to stop the reaction. No purification was performed on the final product.

Methyl ricinoleate: δ (ppm): 0.82 (C18, -CH₃, 3H, t); 1.24 (C4-C7, C14-C17, CH₂, 16H, m); 1.39 (C13, CH₂, 2H, m); 1.55 (C3, CH₂, 2H, m); 1.90 (OH, 1H, s); 1.98 (C8, CH₂, 2H, m); 2.15 (C11, CH₂, 2H, t); 2.23 (C2, CH₂, 2H, m); 3.5 (C12, CH, 1H, m); 3.6 (OCH₃, 3H, s); 5.36 and 5.46 (C10 and C9, -CH=CH-, 1H and 1H, m)

Polyricinolate: δ (ppm): 0.82 (C18, -CH₃, 3H, t); 1.24 (C4-C7, C14-C17, CH₂, 16H, m); 1.45 (C13, CH₂, 2H, m); 1.55 (C3, CH₂, 2H, m); 1.94 (C8, CH₂, 2H, m); 2.2 (C2 and C11, CH₂, CH₂, 4H, m); 3.6 (OCH₃, 3H, s); 4.81 (C12, CH, 1H, m); 5.27 and 5.38 (C10 and C9, -CH=CH-, 1H and 1H, m)

Methyl-12-hydroxystearate: δ (ppm): 0.84 (C18, -CH₃, 3H, t); 1.23 (C4-C10, C14-C17, CH₂, 22H, m); 1.39 (C11 and C13, CH₂, CH₂, 4H, m); 1.58 (C3, CH₂, 2H, m); 2.26 (C2, CH₂, 2H, m); 3.54 (C12, CH, 1H, m); 3.62 (OCH₃, 3H, s)

Polyhydroxystearate: δ (ppm): 0.84 (C18, -CH₃, 3H, t); 1.23 (C4-C10, C14-C17, CH₂, 22H, m); 1.39 (C11 and C13, CH₂, CH₂, 4H, m); 1.58 (C3, CH₂, 2H, m); 2.26 (C2, CH₂, 2H, m); 4.86 (C12, CH, 1H, m)

Characterization

Nuclear Magnetic Resonance (NMR)

All the ¹H and 1D ¹³C-NMR (DEPT) spectra were recorded on Bruker Avance 400 spectrometer (400 MHz and 100.63 MHz for ¹H and ¹³C, respectively) by using CDCl₃ as a solvent at room temperature. ¹H NMR analyses were performed with 16 scans. Multiplicity dependent 1D ¹³C-NMR experiment (DEPT) was performed with deptsp135 pulse program (256 scans) Two-dimensional analysis such as ¹H-¹H COSY (COrrrelation SpectroscopY) was also performed on the same spectrometer.

Size Exclusion Chromatography in THF (SEC)

Polymer molecular weights were determined by Size Exclusion Chromatography (SEC) using tetrahydrofuran (THF) as the eluent. Measurements in THF were performed on an Ultimate 3000 system from Thermoscientific equipped with diode array detector DAD. The system also includes a multi-angle light scattering detector MALS and differential refractive index detector dRI from Wyatt technology. Polymers were separated on three G2000, G3000 and G4000 TOSOH HXL gel columns (300 x 7.8 mm) (exclusion limits from 1000 Da to 400 000 Da) at a flowrate of 1 mL.min⁻¹. Columns temperature was held at 40°C. Polystyrene was used as the standard.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) measurements were performed on DSC Q100 (TA Instruments). The sample was heated from -130 °C to 150 °C at a rate of 10 °C.min⁻¹. Consecutive

cooling and second heating run were also performed at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The glass transition temperatures (T_g) and melting temperatures (T_{melt}) were calculated from the second heating run. Crystallization temperatures (T_{Crys}) were calculated from the cooling run.

Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed on TGA-Q500 system from TA instruments at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere from room temperature to 600°C .

Rheological measurements

The complete methodology is described in supporting information. Rheological measurements were monitored using an Anton Paar Physica MCR302 operating in the parallel plates geometry (diameter 8mm). The measurements were performed under nitrogen flow in the environmental chamber to avoid potential moisture effects. The temperature was controlled by Peltier device and the gap between plates was fixed at 1 mm. Samples were loaded at room temperature. The sample was stabilized at the desired temperature for 5 min before the measurement started.

Preparation of oil blended with viscosity modifiers (additives)

Viscosity modifiers were dissolved in the mineral or organic base oils at the concentration of 3 wt.%. The mixture was heated at $100\text{ }^{\circ}\text{C}$ overnight under magnetic stirring to promote the solubilization and then cooled down without stirring at room temperature for 24 hours. The solubility of the additive in the oil was evaluated macroscopically. Samples were degassed under vacuum and magnetic stirring for 30 minutes right before viscosity measurement using a by LOVIS 2000 densimeter-viscometer.

Viscosity measurements

The viscosimetric tests were performed on a LOVIS 2000 apparatus from Anton Paar at several temperatures: $20\text{ }^{\circ}\text{C}$, $40\text{ }^{\circ}\text{C}$, $60\text{ }^{\circ}\text{C}$, $80\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$. Around 3 mL of solution were added in the

densimeter cell and the capillary tube (\varnothing 1.8 mm for oils and \varnothing 1.59 mm for dodecane) containing a steel ball (\varnothing 1.5mm, $d=7.68 \text{ g.cm}^{-3}$). The density, d , apparent viscosity, η (mPa.s) and the kinematic viscosity, ν ($\text{mm}^2.\text{s}^{-1}$), with $\nu = \eta/d$, are determined directly from the apparatus. The relative viscosity, η_r , was then calculated following equation 1.

$$\eta_r = \frac{\eta}{\eta_0} \text{ Eq. 1}$$

The relative viscosity, i.e. the viscosity of a system “additive in oil” (η) divided by the viscosity of the oil alone (η_0), is used to evaluate the contribution of an additive to the viscosity of a solution. It allows to estimate the thickening efficiency of this additive.

The kinematic viscosities at 40 °C, $\nu_{40^\circ\text{C}}$, and 100 °C, $\nu_{100^\circ\text{C}}$, were used to calculate the Viscosity Index (VI) according to Eq. 2 ASTM D 2270-10.²⁹

$$\text{VI} = \frac{\nu_{100^\circ\text{C}}}{\nu_{40^\circ\text{C}}} \text{ Eq. 2}$$

The Q factor, defined according to equation 3, were calculated from specific viscosities η_{sp} , at 40 °C and 100 °C, obtained according to equation 4.

$$Q = \frac{\eta_{sp\ 100^\circ\text{C}}}{\eta_{sp\ 40^\circ\text{C}}} \text{ Eq.3 with } \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \text{ Eq.4}$$

The Q value is the ratio between the specific viscosities at 40°C ($\eta_{sp\ 40^\circ\text{C}}$) and at 100°C ($\eta_{sp\ 100^\circ\text{C}}$). Specifically, $0 < Q < 1$ indicates that the thickening power of the additive is less significant at 100°C than at 40°C. Conversely, Q values > 1 indicate the thickening power is more prominent at high temperature. The highest the Q value, the highest the additive capability to reduce the oil viscosity loss at high temperature.

Results and discussion

Syntheses of polyricinoleate and polyhydroxystearate within a broad range of molecular weights

Polyricinoleate and polyhydroxystearate were synthesized by polycondensation of methyl ricinoleate and methyl-12-hydroxystearate, respectively. Different molecular weights were targeted. Consequently, the choice of precursors, as well as the reaction conditions, were investigated to obtain high molecular weight polyester. Both A-B monomers were selected with a grade of purity above 99% in order to limit secondary reaction and polymerization termination due to the presence of impurities.

According to the literature, in the case of transesterification with hydroxyl-ester interchange reaction, $\text{Ti}(\text{OiPr})_4$ is largely described as a very efficient catalyst leading to high molecular weight polyesters³⁰⁻³² and notably for the synthesis of poly(ethylene naphthalate)³³, poly(ethylene terephthalate)^{30,34} and, more recently, linear bio-based polyesters^{32,35,36}. Consequently, this organometallic catalyst was selected. A temperature of 180 °C was chosen as a good compromise between high catalytic activity and the limitation of transfer reactions and terminations (especially due to the carbon-carbon double bond in the case of methyl ricinoleate). Finally, polymerization was performed in bulk, thus avoiding further treatment to remove the solvent. However, the high viscosity of the polymerization medium tends to slow down the polymerization process and limit the reaction extent. In order to overcome this issue, a mechanical stirring was used during polymerization process when high molecular weights PRic or PHS were targeted. Polyesters were then analyzed without further purification.

The structures of the polyesters were confirmed by ^1H NMR in agreement with previous publication¹⁵ (see Figure 2 for PRic and Figure SI-1-3 in Supporting Information for PHS).

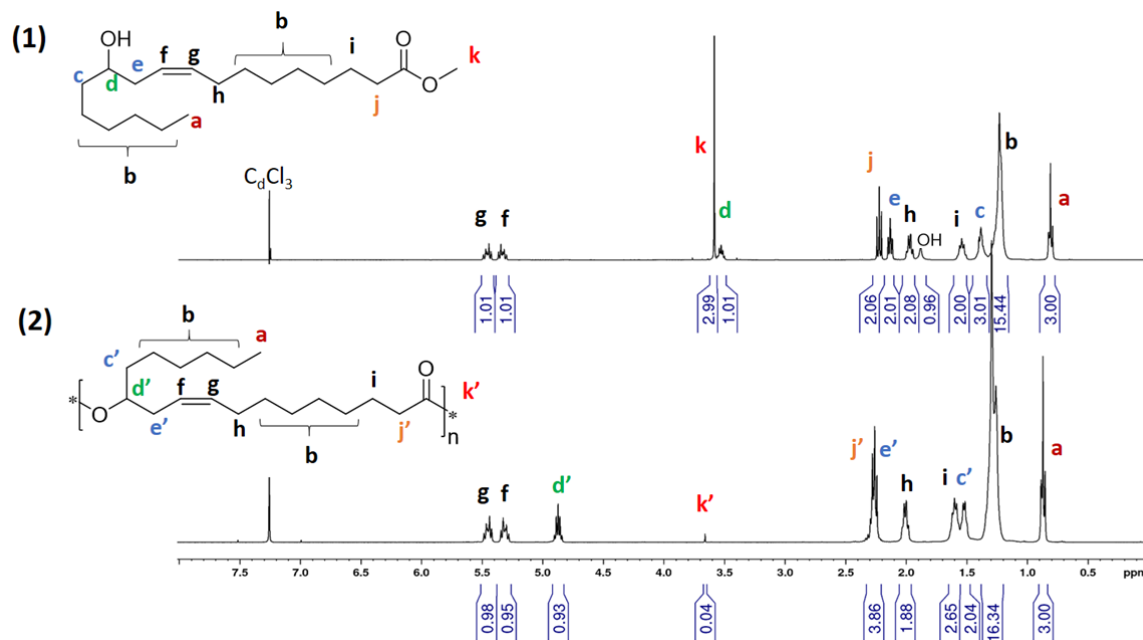


Figure2: ^1H NMR spectra of (1) methyl ricinoleate monomer and (2) polyricinoleate in CDCl_3

In both cases, the peak at 0.82 ppm, representative of the terminal CH_3 protons of the fatty methyl esters, is used as a reference. The polycondensation is confirmed by the drastic decrease of the characteristic methoxy peak at 3.59 ppm and the shift of the peak corresponding to the proton in α position of the OH group from 3.5 to 4.88 ppm. The protons in α and β positions of the ester group are assigned at 2.26 ppm and 1.6 ppm, respectively. In the case of polyricinoleate, there is also a small shift of the protons in β position of the OH group, from 1.40 ppm to 1.55 ppm and 2.15 ppm to 2.26 ppm.

Table 2: Reaction extent (p), degree of polymerization (DP_n), molecular weights and solubility in mineral oil (MO) or organic triglyceride oil (OTO) of a series of PRic and PHS

Entry	Time (h)	p^1	DP _n ¹	M _n ¹ (g.mol ⁻¹)	M _n ² (g.mol ⁻¹)	M _w ² (g.mol ⁻¹)	\mathcal{D}^2	Sol. in MO ³	Sol. in OTO ³
PRic-1 ^a	6	0.894	9.4	3000	4000	6100	1.5	Yes	Yes
PRic-2 ^a	8	0.902	10.2	4200	7200	10600	1.5	Yes	Yes
PRic-3 ^a	24	0.977	45	12400	18200	32200	1.7	Yes	No
PRic-4 ^a	48	0.984	63	19800	21700	47100	2.2	No	No
PRic-5 ^b	48	0.991	110	34000	28100	131500	4.6	No	No
PHS-1 ^a	8	0.960	25	7700	8100	17500	2.1	Yes	Yes
PHS-2 ^a	48	0.990	100	30200	24000	68100	2.4	Yes	Yes
PHS-3 ^b	48	0.996	225	60000	28500	78400	2.5	Yes	Yes

Reaction conditions: 180°C, 1wt.% of Ti(OiPr)₄ in the melt under vacuum, 200 rpm

a: Magnetic stirring and b: mechanical stirring

1 Obtained by ¹H NMR using OCH₃ peak at 3.6 ppm for calculation

2 $\mathcal{D} = M_w/M_n$, dispersity. Obtained by SEC in THF – triple detection, dn/dc values used for calculation

3 Polymer solubility at 3wt% in oil after one night heated at 100°C under stirring and 24 hours at 20°C

As indicated in Table 2, molecular weights of PRic and PHS were impacted by the polymerization duration and mode of stirring. SEC traces (Figure SI-4, see Supporting Information) shows the standard step-growth polymerization profiles with a molecular weight distribution shifting to the higher molecular weights with time. M_n values obtained by SEC analysis using triple detection are in agreement with the ones determined by ¹H NMR using chain-end analysis. PHS-3 is the only exception where M_n predicted by Carothers equation is twice the

one obtained by SEC. This may be due to secondary reactions, such as cyclization, that decrease the concentration of terminal methyl esters. In the case of PRic, a broad range of molecular weights was obtained from $M_w = 6 \text{ kg}\cdot\text{mol}^{-1}$ to $M_w = 131 \text{ kg}\cdot\text{mol}^{-1}$ (17 and $78 \text{ kg}\cdot\text{mol}^{-1}$ for PHS) which is the highest molecular weight reported in literature to the best of our knowledge.¹³⁻¹⁵ While all polyesters exhibit a dispersity close to 2 as it is expected, the dispersity around 4.6 for PRic-5 suggests the occurrence of side reactions. Indeed, while a small fraction of oligomers can be detected whatever the final molecular weight distribution, in the case of PRic-5, this fraction is more intense leading to higher dispersity. This peak may be due to a backbiting reaction leading to the formation of ricinoleate lactone. Since there is no apparent broadening of the polymer peak (see Figure SI-4) the presence of this oligomeric fraction explains the dispersity value obtained.

Thermal properties

The thermal stabilities of the PRic and PHS were investigated by thermogravimetric analyses (TGA), under a nitrogen stream at a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The polymer degradation temperatures at 5 wt.% are reported in Table 3. Compared to both monomers which begin to degrade at $160 \text{ }^\circ\text{C}$, the thermal stability of the polymer is higher with a degradation above $300 \text{ }^\circ\text{C}$ for all the polyesters. PHS possesses slightly better thermal stability compared to PRic which can be explained by the presence of unsaturation in the backbone. No influence of the polyester molecular weights on the temperature of degradation can be noticed.

PRic and PHS were also analyzed by differential scanning calorimetry analysis, traces of which are displayed in Figure 3. The glass transition temperature, T_g , the crystallization temperature, T_{cris} , the melting temperature, T_{melt} and corresponding enthalpies were recorded after the second heating scan at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. All the results are reported in Table 3.

Table 3: Thermal behavior of PRic and PHS determined by TGA and DSC

Entry	M_n^1 (g.mol ⁻¹)	M_w^1 (g.mol ⁻¹)	D^1	$T_{d5\%}^2$ (°C)	T_g^3 (°C)	T_{melt}^3 (°C)	ΔH_m^3 (J/g)	T_{cris}^3 (°C)	ΔH_c^3 (J/g)
MRic	-	-	-	160	-	-7	79	-41	28
PRic-1	4000	6100	1.5	296	-77	-	-	-	-
PRic-2	7200	10600	1.5		-71	-	-	-	-
PRic-3	18200	32200	1.7	303	-69	-	-	-	-
PRic-4	21700	47100	2.2		-68	-	-	-	-
PRic-5	28100	131500	4.6	300	-68	-	-	-	-
MHS	-	-	-	160	-	54	235	47	201
PHS-1	8100	17500	2.1	307	-37	-20	30	-31	30
PHS-2	24000	68100	2.4	309	-44	-22	22	-33	29
PHS-3	28500	78400	2.5	314	-41	-22	27	-34	25

1 Obtained by SEC in THF – triple detection, dn/dc values using for calculation

2 Temperature for 5wt% degradation- Obtained by TGA

3 Obtained by DSC- Second heating cycle at a rate of 10°C min⁻¹

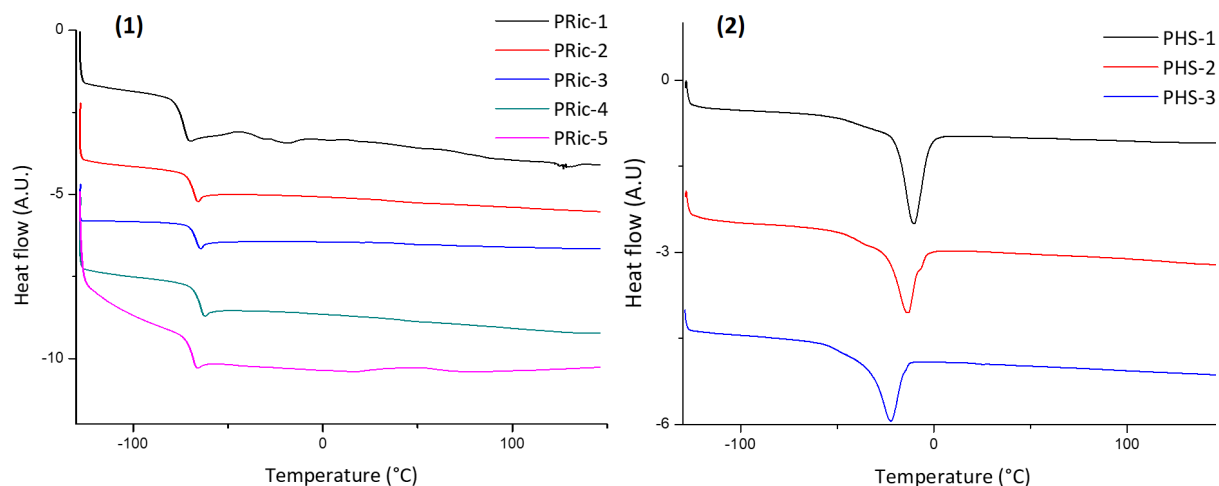


Figure 3: DSC traces of (1) PRic and (2) PHS with both several molar masses. Second heating cycle rate of 10 °C.min⁻¹

While the two polymer structures are identical except the presence of a double bond in *cis* configuration along the polymer backbone, the thermal behavior of PRic and PHS are dramatically different. On the first hand, polyhydroxystearate shows a semi-crystalline behavior with a melting temperature of about -20 °C with a T_g around -40 °C. On the other hand, PRic behaves as a completely amorphous polymer with a low T_g close to -70°C. PRic T_g values follow the Fox-Flory law (see equation 4) with respect to molecular weights (see Figure SI-3, in Supporting Information).³⁷

$$T_g = T_{g,\infty} - \frac{K}{M_n} \quad \text{Eq. 4}$$

with, $T_{g,\infty}$ is the maximum glass transition temperature that can be reached at a theoretical infinite molecular weight and K a parameter related to the contribution of the chain-end to the free volume. For PRic, experimental T_g fits with the following values: $T_{g,\infty} = -66$ °C and $K = 4.1 \cdot 10^4$ g.mol⁻¹. In the case of PHS, no effect of the molecular weight on the T_g was observed since the glass transition is controlled by the crystal phase.

Impact of PRic molar masses on its melt rheological behavior

As expected, PRic viscosity depends on its molecular weight. Indeed, at room temperature, PRic-1 ($M_w = 6\,100$ g.mol⁻¹) behaves as a viscous liquid while PRic-5 ($M_w = 131\,000$ g.mol⁻¹) does not flow at short time scale and appears as a viscoelastic solid. This observation suggests a strong effect of the molecular weight on the rheological properties of polyricinoleate. This effect can be quantified through the measurement of η_0 , the Newtonian viscosity.

As it was established by Fox and Flory³⁸, the viscosity of a polymer is strongly related to its molecular weight. This relationship varies whether the polymer is entangled or not, according to equation 5 and equation 6.

$$\log \eta_0 = \log Mw + A \text{ for } M < M_c \quad \text{Eq.5}$$

$$\log \eta_0 = 3.4 \log Mw + B \text{ for } M > M_c \quad \text{Eq. 6}$$

where η_0 is the Newtonian viscosity and M_c the critical molecular weight of entanglement. A and B are empirical constants dependent on the nature of the polymer and the temperature.

By rheometry analysis (see Supporting Information), Newtonian viscosities at 20°C was determined for a new PRic series with Mw ranging from 5 000 to 130 000 g.mol⁻¹, and plotted as a function of the PRic molecular weight (see Figure 4, and Table 4).

Table 4: Molecular weights and melt Newtonian viscosity at 20°C

Entry	M_n^1 (g.mol ⁻¹)	M_w^1 (g.mol ⁻¹)	\bar{D}^1	η_0 20°C (Pa.s) ²
PRic-6	3 000	5 000	1.7	6.9 ± 0.5
PRic-7	8 000	18 000	2.2	28.81 ± 0.028
PRic-8	11 000	31 000	2.8	872 ± 3.7
PRic-9	15 000	92 000	6.1	2.60 10 ⁵ ± 6.4 10 ³
PRic-10	28 000	131 500	4.6	8.53 10 ⁵ ± 8.2 10 ⁴

1 Obtained by SEC in THF – triple detection, dn/dc values used for calculation

2 See Supporting Information for more information about the determination of η_0

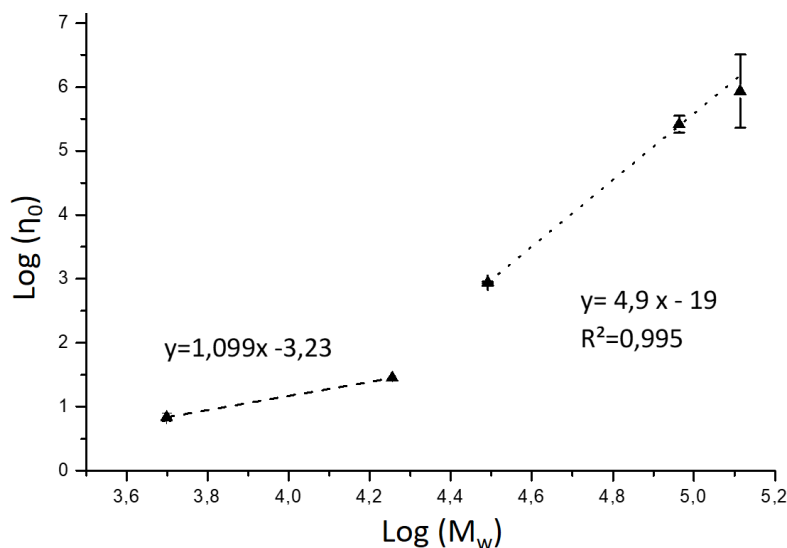


Figure 4: Log-log plot of the Newtonian viscosity versus molar mass for PRic samples at 20 °C

As expected, η_0 increases with the PRic molecular weight, from 6.87 Pa.s (5 000 g.mol⁻¹) to 8.53 10⁵ Pa.s (131500 g.mol⁻¹). A slope rupture is clearly observed for $\log(M_w) \approx 4.3$ corresponding to molar weight around $M_w = 25\,000$ g.mol⁻¹. For $M_w < 25\,000$ g.mol⁻¹, a slope of 1 is obtained suggesting that the chains are disentangled (PRic-6 and PRic-7) and probably present Rouse relaxation mode. For $M_w > 25\,000$ g.mol⁻¹, a slope around 4.9 is obtained. This is superior to the theoretical value for entangled polymer chains, i.e. 3.4. whose dynamic is governed by reptation. The large dispersity of PRic-9 ($\mathcal{D} = 6.1$) and PRic-10 ($\mathcal{D} = 4.6$) could explain the discrepancy between the experimental and the theoretical value of 3.4. Indeed, it is reported that dispersity has an impact on the rheological behavior of the polymer chains and, consequently, on the sample viscosity.^{39,40} However, as reported in the literature, this effect implies variation from 3.3 to 3.7.⁴¹⁻⁴³ There is also probably an impact of the pendant alkyl segments along the polymer backbone (comb-like structure).^{40,44}

Towards promising viscosity modifiers

All the so-formed PRic and PHS were then tested as additives in a mineral oil (MO) and an organic triglyceride oil (OTO) to be evaluated as viscosity modifiers for lubricants. A concentration of 3 wt.% was fixed. As reported in Table 2, the PRic with the highest molecular weights are not soluble in the oils: PRic-3 to 5 for MO, PRic-4 and 5 for OTO. Surprisingly, polyhydroxystearate is perfectly soluble in both oils, whatever the molecular weights. Only the oils containing soluble PRics of PHS as additives were then analyzed by viscosimetry. The kinematic viscosity of the mixtures was measured from 20 °C to 100 °C allowing determining the relative viscosity and the Viscosity Indexes. The relative viscosity versus the temperature is displayed in Figure 5 and the kinematic viscosities, the VI as well as the Q values are reported in Table 5. Their values were compared to two commercial additives, Ref-O, specific for the organic oil and Ref-M, specific for the mineral one.

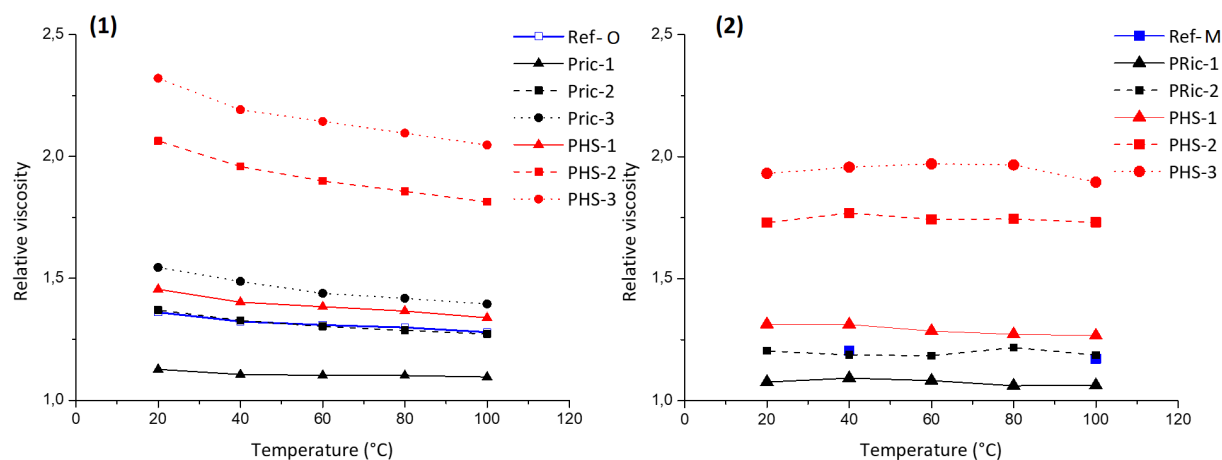


Figure 5: Relative viscosities of several PRic, PHS and commercial additives blended at 3 wt.% in (1) organic oil and (2) mineral oil regarding the temperature between 20 °C and 100 °C.

The most significant impact on the relative viscosity is related to the polymer molecular weights. The highest the molecular weight, the highest the relative viscosity. The PHS-3 with a $M_w = 80$

$\text{kg}\cdot\text{mol}^{-1}$ shows the best thickening properties with an increase of the kinematic viscosity from 20 $\text{mm}^2\cdot\text{s}^{-1}$ to 45 $\text{mm}^2\cdot\text{s}^{-1}$ in OTO and from 19 $\text{mm}^2\cdot\text{s}^{-1}$ to 37 $\text{mm}^2\cdot\text{s}^{-1}$ in MO at 40 °C for 3 wt.% blend. These results point out that high molecular weight PHS is a promising thickener in both oils tested.

The addition of a polymer additive in OTO induced a decrease of the relative viscosity with the temperature. This phenomenon is observed for all the polyesters tested, independently of their chemical composition and molecular weight leading to value of Q below 1 testifying that thickening power of the additive is less significant at 100°C than at 40°C. In the case of PHS, a slight increase of Q was observed with the molecular weight, while the Q values tend to decrease with PRic molecular weights. However, the Viscosity Index is significantly increased by the addition of a polymer additive in the oil. Even the blend with the lowest molecular weight PRic led to a significant VI increase from 152 to 163. In these conditions, whatever PHS molecular weight, the Viscosity Index is better than with the commercial additive tested. A maximum of VI = 204 is obtained for the oil blended with PHS-3 corresponding to a VI increase of +52. All these results demonstrate that PHS-3 could also be used as a Viscosity Index improver of OTO.

For MO, the Q values appears to increase with the molecular weights with values close to 1 for PRic-2 (Q=0.99) and PHS-3 (Q=0.94). These indicate a more stable viscosity with temperature which leads to better VI with less increase in the kinematic viscosity. For example, in the case of PRic-2, same VI were obtained for OTO and MO but in the first case kinematic viscosity at 40°C is increased by 33% compared to only 19% for MO.

a

Table 5: Kinematic viscosity, KV, at 40 and 100 °C VI and Q values of OTO and MO blended with 3 wt.% of commercial additives, PRic and PHS polymers.

	At 3wt% in OTO				At 3wt% in MO			
	KV 40°C	KV 100°C	VI	Q	KV 40°C	KV 100°C	VI	Q
None	20.55	4.67	152	-	18.71	4.34	145	-
Ref	27.19	5.98	175	0.87	22.55	5.08	163	0.84
PRic-1	22.73	5.12	163	0.90	20.45	4.61	147	0.69
PRic-2	27.29	5.94	172	0.83	22.23	5.15	172	0.99
PRic-3	30.57	6.52	175	0.81	-	-	-	-
PHS-1	28.82	6.25	176	0.84	24.56	5.49	171	0.85
PHS-2	40.24	8.47	195	0.85	33.1	7.51	205	0.93
PHS-3	45.05	9.56	204	0.88	36.62	8.22	209	0.94

Conclusion

Polyricinoleate and polyhydroxystearate were synthesized using $Ti(OiPr)_4$ as a catalyst within a large range of molecular weights, from $M_w = 3 \text{ kg.mol}^{-1}$ up to $M_w = 130 \text{ kg.mol}^{-1}$ in the case of PRic. The obtained PHS appeared to be semi-crystalline with a melting point around $-20 \text{ }^\circ\text{C}$ while PRic was amorphous with a glass transition temperature around $-70 \text{ }^\circ\text{C}$ due to the presence of an internal unsaturation in its backbone. The PRic rheological behavior was evaluated as a function of its molecular weight. It appears that, for low M_w , PRic behaves as a viscous material. Above $M_w = 25 \text{ kg.mol}^{-1}$, its melt viscosity increases drastically due to the formation of entanglements.

Finally, PRic and PHS have been tested as viscosity modifiers. Contrary to PHS, due to a lack of solubility for the highest molecular weights, only PRic with $M_w \leq 10 \text{ kg.mol}^{-1}$ and $M_w \leq 32 \text{ kg.mol}^{-1}$ could be tested in mineral and organic oil, respectively. Both PRic and PHS have a

thickening effect in oil, but PHS with $M_w = 80 \text{ kg}\cdot\text{mol}^{-1}$ showed particularly good thickening efficiency by doubling the viscosity of both OTO and MO and by increasing the Viscosity index about + 52 and +64, respectively. As a result, the bio-based PHS with high molecular weights could be considered as promising viscosity modifiers for more environmentally friendly lubricant applications.

Supporting Information.

The following files are available free of charge: NMR of PHS, SEC traces of PRic and PHS, rheology methodology and results..

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. HM performed the experiments, JFLM performed the rheology analysis.

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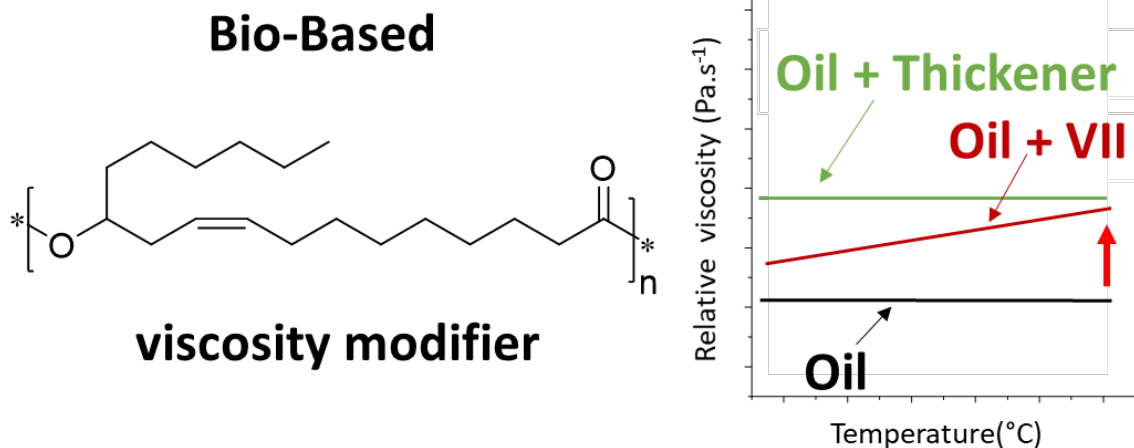
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For Table of Contents Use Only



Polyester obtained by self polyesterification of ricinoleate derivatives were synthesized. Their properties in melt and oil solution were investigated in regards to their molecular weights.

Supporting information

Bio-based polyricinoleate and polyhydroxystearate: properties and evaluation as viscosity modifiers for lubricants

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Table SI-1: Translation factor and activation energy obtained by TTS master curves at -20°C.

Table SI-2: Translation factor and activation energy obtained by TTS master curves at 80°C as reference.

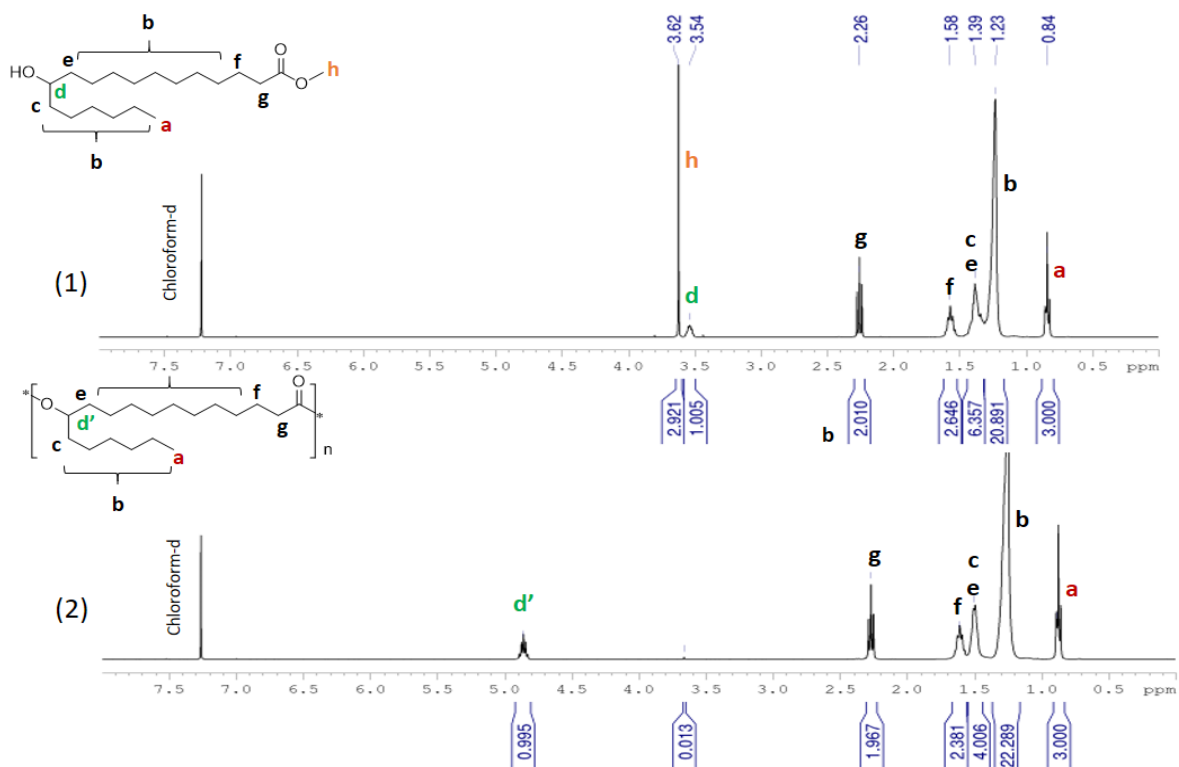


Figure SI - 2: ^1H NMR spectra of (1) methyl-12- hydroxystearate monomer and (2) polyhydroxystearate in CDCl_3

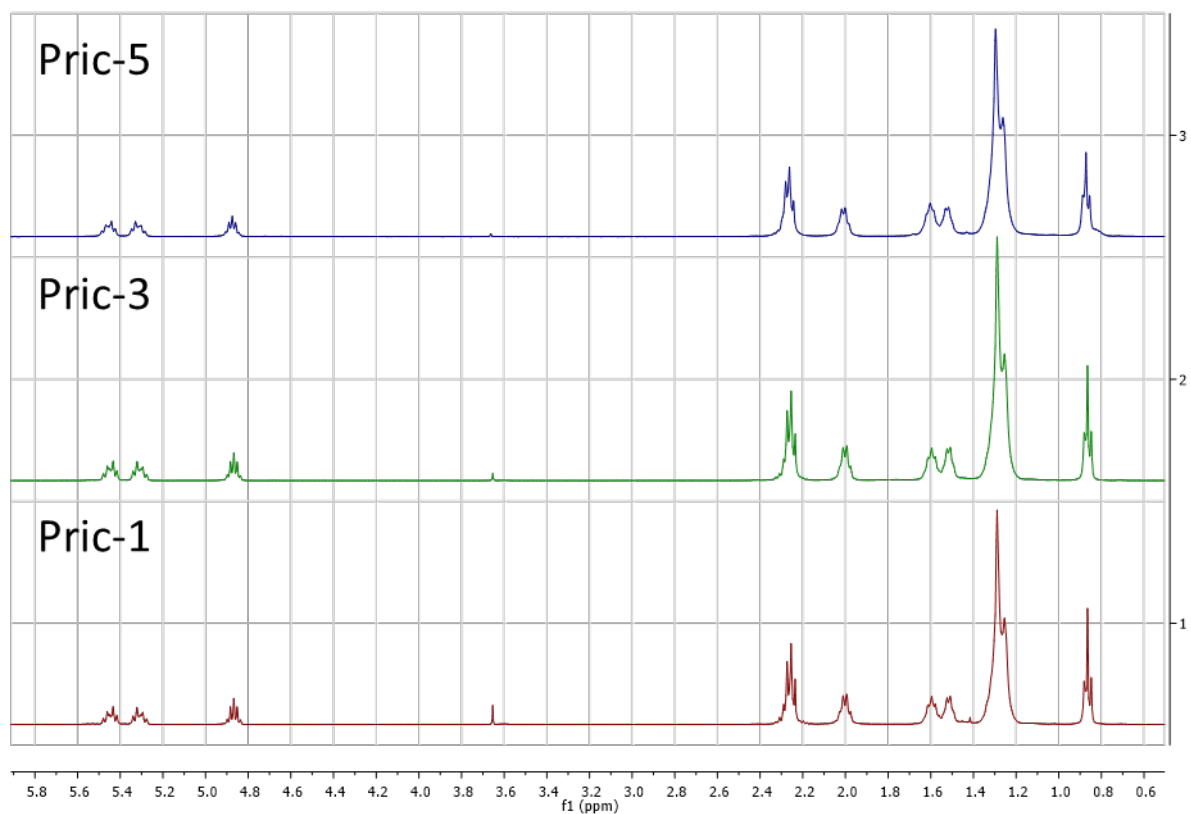


Fig SI – 2: ¹H NMR spectra of polyricinoleate in CDCl₃

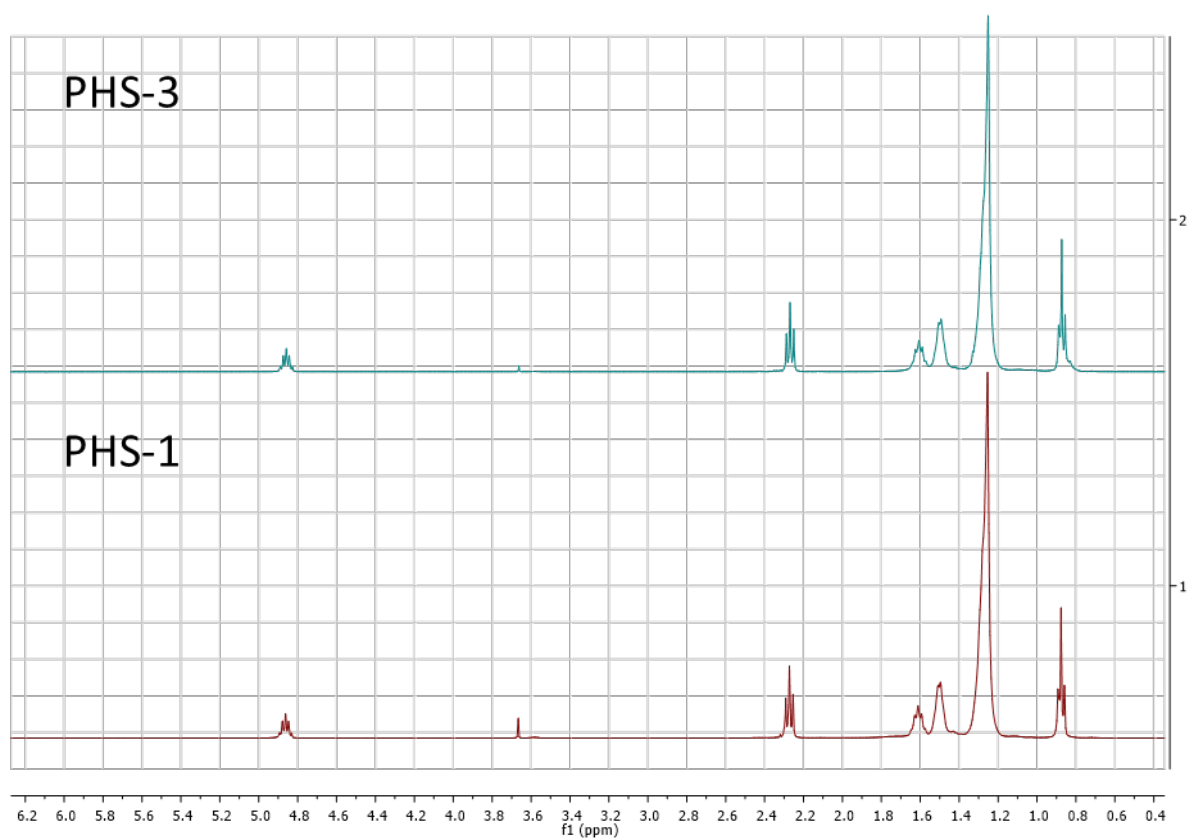


Figure SI - 3: ¹H NMR spectra of polyhydroxystearate in CDCl₃

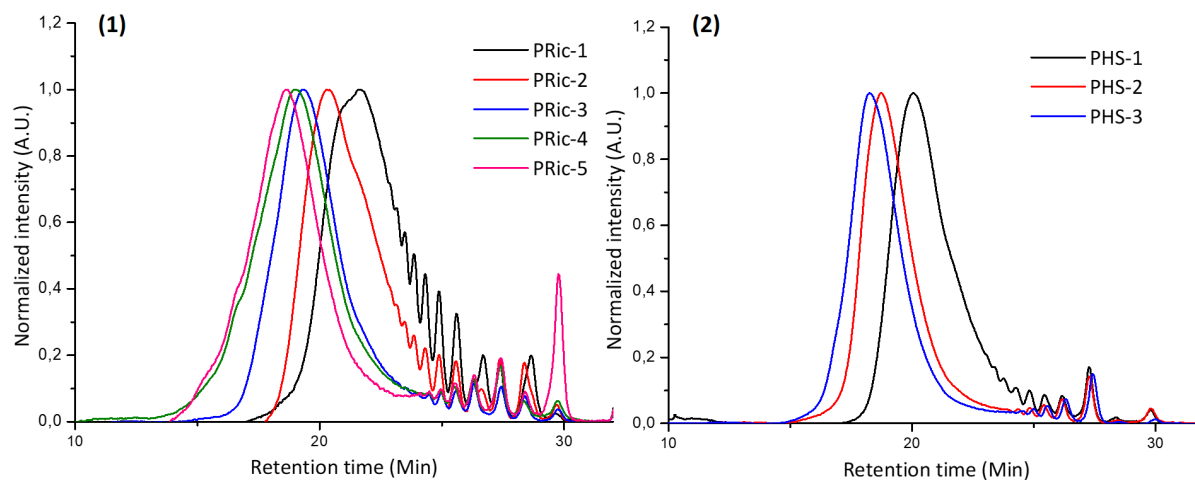


Figure SI - 4: SEC traces of (1) Polyricinoleate and (2) Polyhydroxystearate. Measurement performed in THF.

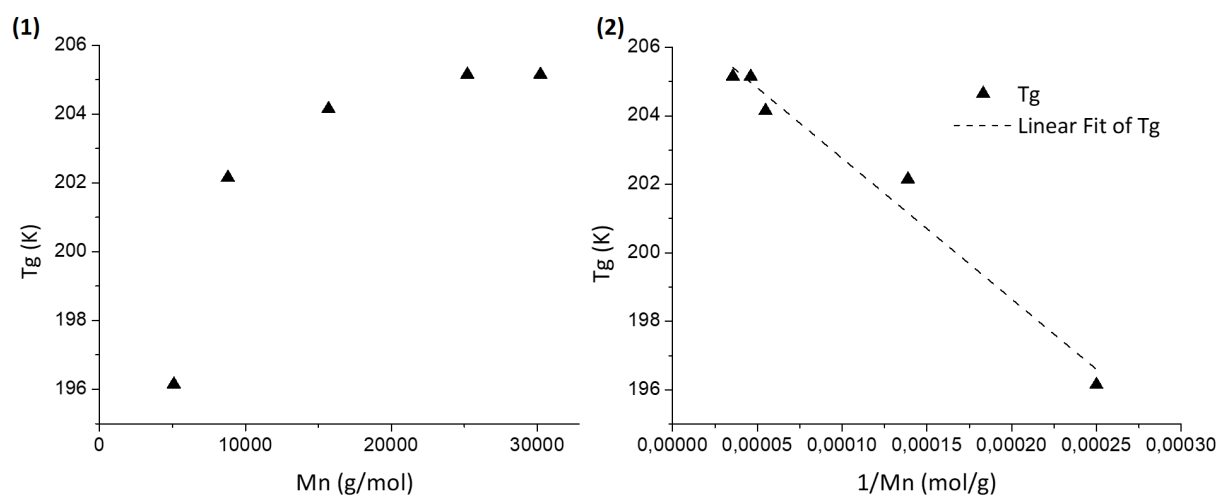


Figure SI - 5: PRic glass transition temperature as a function of (1) PRic molecular weight (M_n) and (2) $1/M_n$

Rheometry analysis:

Methodology

The objective was to establish the evolution profile of the newtonian viscosity versus molecular weight of the different system at a fixed, reference temperature. Viscosity was estimated through the evaluation of complex viscosity η^* measured at different temperature, and the establishment of master curves through the use of the Time Temperature Superposition (TTS).

The complex viscosity was calculated with the data obtained from the dynamic shear measurements according to equation 1.¹

$$|\eta^*| = \frac{|G^*|}{\omega} = \frac{\sqrt{(G')^2 + (G'')^2}}{\omega} \quad \text{Eq.1}$$

where the elastic modulus G' and the loss modulus G'' are given as a function of the angular frequency ω .

According to Cox-Merz Rule,¹ the dependence of the steady shear viscosity on the shear rate is equal to the dependence of the complex viscosity as a function of frequency. Therefore a plateau of complex viscosity at low angular frequencies reflects the Newtonian viscosity. In some cases, when the plateau value of complex viscosity could not be obtained with the master curves, creep experiments have then been performed to measure the viscosity.

The shift factor $a_{T/T_{ref}}$ used to establish master curves follows an Andrade law¹ according to Equation 2, as illustrated in the Figure SI 6

$$\ln(a_T) = \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{Ref}} \right) \quad \text{Eq.2}$$

where E_a is the activation energy and R the universal gas constant. By using Andrade law, it is possible to determine the viscosity of the material at another temperature, as, the translation factor a_T is correlated to the melt polymer viscosity.² and can be considered as the ratio of viscosity at two different temperature (eq 3).

$$a_T = \frac{\eta_T}{\eta_{T_{Ref}}} \quad \text{Eq.3}$$

Then, the Newtonian viscosities could be estimated at 20 °C for all the polymers..

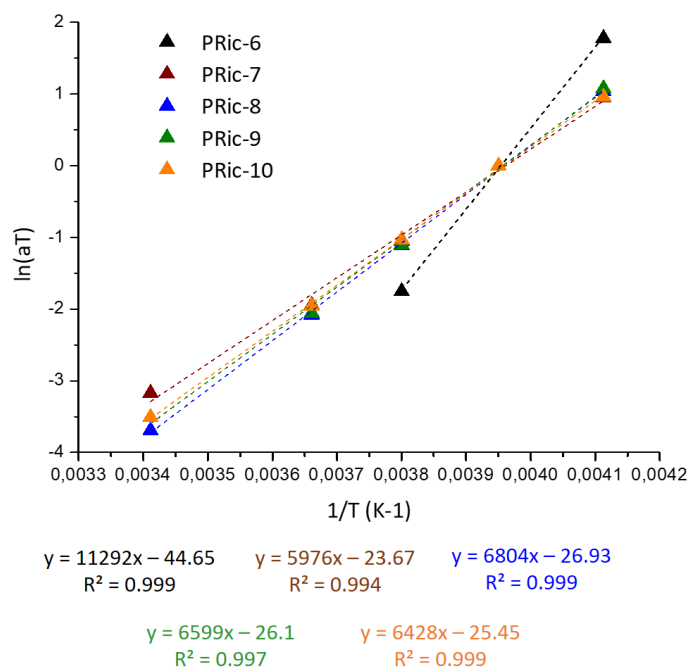


Figure SI - 6: Translation factor as a function of $1/T$ fitted with Andrade law

Rheology results

As displayed in Figure SI-7, first the linear domains of PRic with different molecular weights were determined. For all samples, a linear domain was obtained up to a shear strain of 100%. A shear strain of $\gamma=1\%$ was fixed for the frequency sweep experiments.

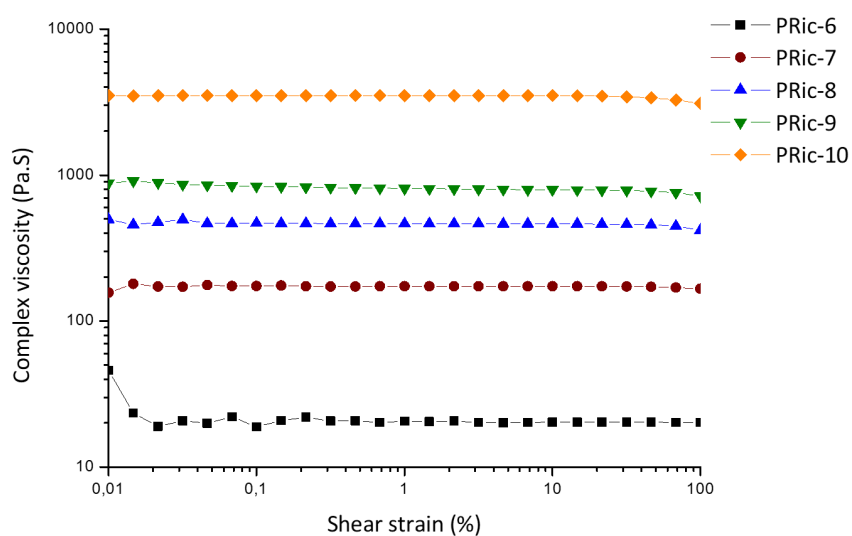


Figure SI - 7: Complex viscosity as a function of shear strain for a series of PRic with various M_w . Performed at 20°C with an angular frequency of $10 \text{ rad}\cdot\text{s}^{-1}$

The rheological properties were evaluated under dynamic frequency sweep (100 rad.s^{-1} - 0.1 rad.s^{-1}) at different temperature and the time-temperature superposition (TTS) principle was applied. The master curves of elastic and loss moduli obtained for a reference temperature of $-20 \text{ }^{\circ}\text{C}$ are plotted in Figure SI-8

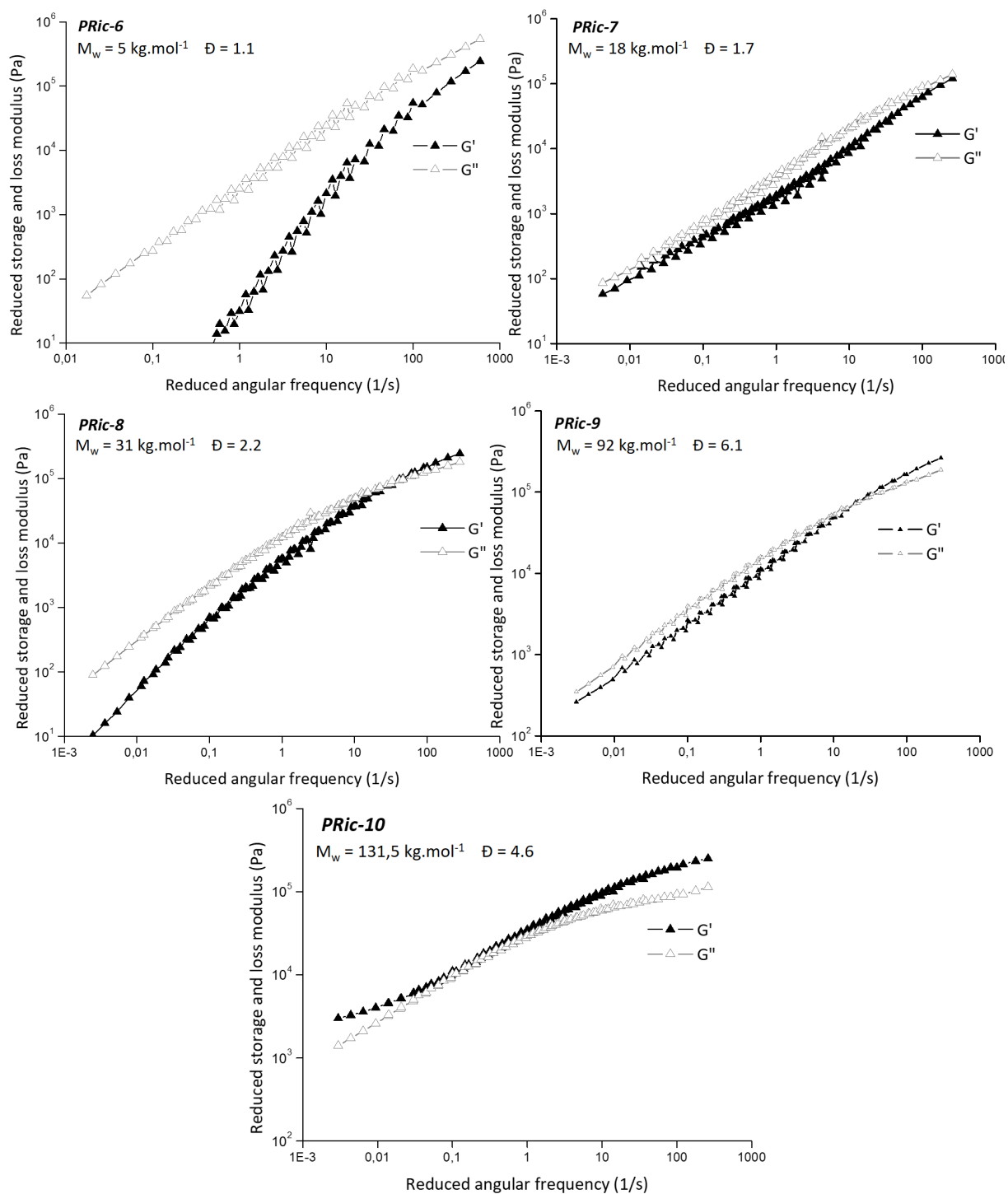


Figure SI - 8: Master curves at -20 °C of PRic samples. storage and loss modulus are expressed versus the reduced angular frequency

From these data, the complex viscosity of the series of PRics were expressed as a function of angular frequency, with $0,003 < \omega < 294 \text{ rad}\cdot\text{s}^{-1}$ at -20 °C. Results are plotted in Figure SI-9.

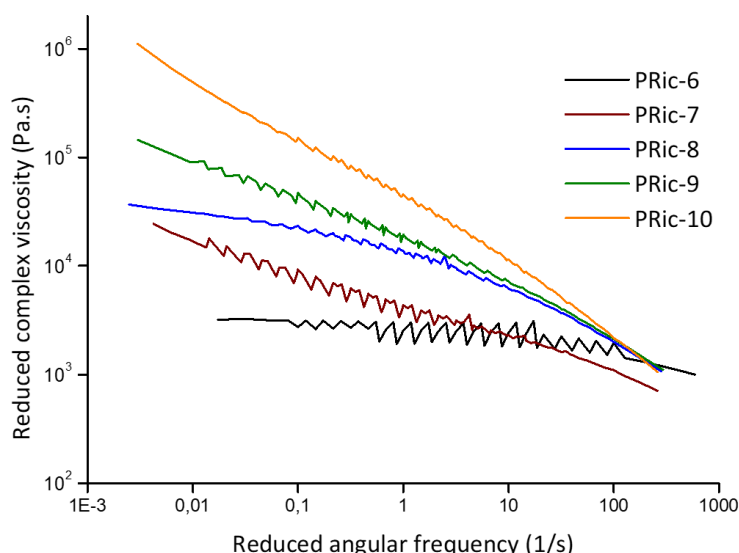


Figure SI - 9: Polycrinoleate reduced complex viscosity versus the reduced angular frequency obtained from TTS at -20°C as reference temperature, 1% shear strain

Regarding the master curves in Figure SI-8, it appears clearly that for most of the polycrinoleate tested, no viscosity plateau is observed at low frequencies, with the noticeable exceptions of PRic-6 and PRic-8. In these two cases, viscosity plateau is observed for $\omega < 1 \text{ rad.s}^{-1}$ in the case of PRic-6 and $\omega < 0.1 \text{ rad.s}^{-1}$ in the case of PRic-8 allowing determination of a Newtonian viscosity at -20°C

$$\text{PRic-6: } \eta^*_{-20^{\circ}\text{C}} = 3010 \pm 230 \text{ Pa s}$$

$$\text{PRic-8: } \eta^*_{-20^{\circ}\text{C}} = 34900 \pm 1500 \text{ Pa s}$$

Then the viscosity could be calculated at 20°C using Andrade law.

For the other PRic samples, the viscosity was not stable with the frequency in the range of frequencies and temperatures tested. Newtonian viscosities were then determined using creep experiments in which several shear stress were applied on the polymer sample and the resulting shear strain was measured as a function of time. Different temperatures were used for each creep experiments, a viscosity and steady state shear rate value were reported. Viscosity obtained was plotted versus the shear rate as displayed in Figure SI-10. The obtained viscosities were almost independent of the the shear rate and thus considered as Newtonian, Although a beginning of shear thinning is detected in PRic-10

$$\text{PRic-7: } \eta_{20^{\circ}\text{C}} = 28.80 \pm 0.03 \text{ Pa.s}$$

PRic-9: $\eta_{200\text{ }^\circ\text{C}} = 124.8 \pm 2.2 \text{ Pa}\cdot\text{s}$

PRic-10: $\eta_{150\text{ }^\circ\text{C}} = 3500 \pm 100 \text{ Pa}\cdot\text{s}$

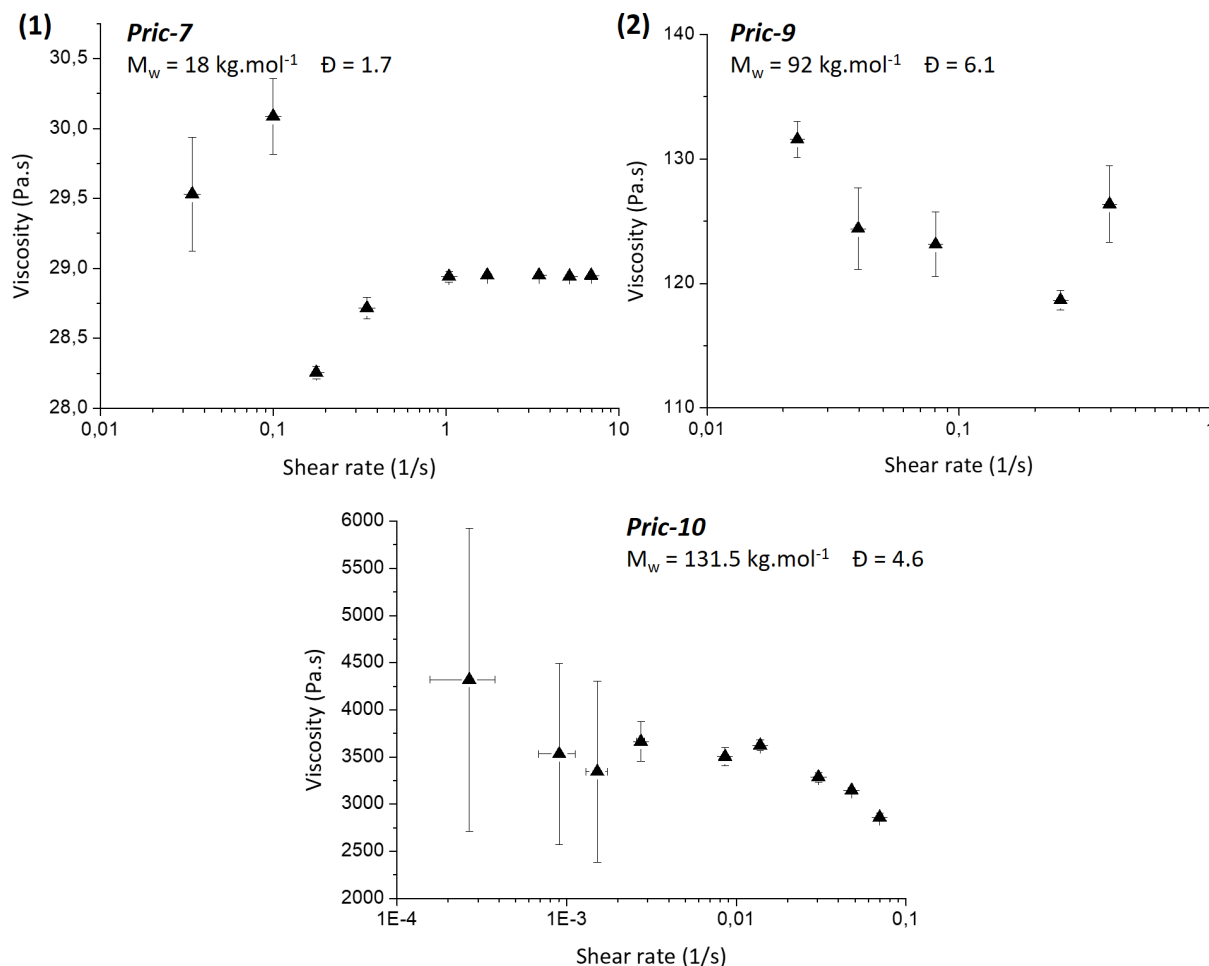


Figure SI - 10: Viscosity versus shear rate obtained by creep measurements. (1) PRic-7 performed at 20 °C, (2) PRic-9 performed at 200 °C and (3) PRic-10 performed at 150 °C

For Pric 8 and Pric 6, the Newtonian viscosity at 20°C were calculated from the value of Newtonian viscosity obtained with master curves of complex viscosity versus frequency at a temperature reference of -20°C. for Pric -7, Pric 9 and Pric 10 Newtonian viscosities were obtained by creep experiments, as they could not be determined through dynamic experiments.. As the temperature chosen for creep experiments of Pric 9 and Pric 10 (200°C and 150°C respectively) were far above the reference temperature of -20°C, another master curve (G' , G'' $f(aT_w)$) have been realized for Pric-9 and Pric-10 at a reference temperature of 80°C and new shift factor aT has been calculated. Again these shift factor obey an Andrade law but slight variation of activation energy compared to the reference temperature of -20°C was obtained

(Table SI-2). We used this activation energy for PRic 9 and Pric 10 to calculate the Newtonian viscosity at 20°C.

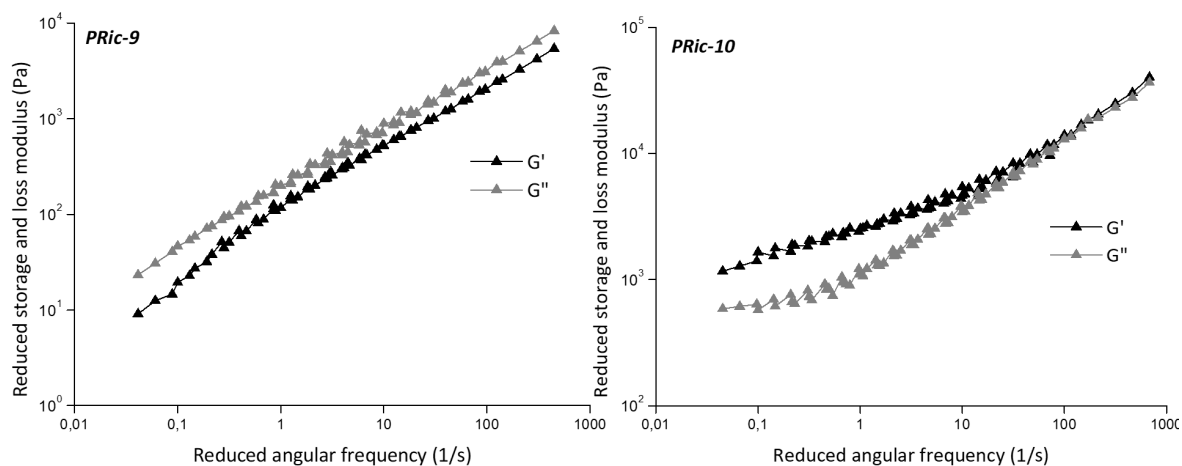


Figure SI-11: Master curves at 80°C of PRic-9 and PRic-10 samples. Reduced storage and loss modulus are expressed versus the reduced angular frequency

Table SI-3: Translation factor and activation energy obtained by TTS master curves at -20°C.

	T (°C)	-30	-20*	-10	0	20	Ea (kJ.mol ⁻¹)
PRic-6	a_T	5.911	1	0.173	-	-	93.72
	$a_{T\text{ calc}}$	6.256	1	0.184	0.038	0.002	
	%error	5.62	0	5.67	-	-	
PRic-7	a_T	2.592	1	0.350	0.143	0.042	49.57
	$a_{T\text{ calc}}$	2.634	1	0.408	0.178	0.040	
	%error	1.74	0	16.97	24.65	5.21	
PRic-8	a_T	2.832	1	0.328	0.125	0.025	56.63
	$a_{T\text{ calc}}$	3.028	1	0.359	0.139	0.025	
	%error	6.93	0	9.41	11.25	2.58	
PRic-9	a_T	2.937	1	0.332	0.128	0.030	54.80
	$a_{T\text{ calc}}$	2.921	1	0.371	0.148	0.029	
	%error	0.531	0	-11.767	-16.115	4.959	
PRic-10	a_T	2.612	1	0.356	0.141	0.030	53.47
	$a_{T\text{ calc}}$	2.846	1	0.380	0.155	0.031	
	%error	8.957	0	-6.996	-10.430	-4.458	

*: Reference temperature - $a_{T\text{ calc}}$ are shift factors from computation using Arrhenius law

Table SI-4: Translation factor and activation energy obtained by TTS master curves at 80°C as reference.

	T (°C)	20	40	60	80*	100	150	200	Ea (kJ.mol ⁻¹)
PRic-9	a_T	30.457	8.497	2.6867	1	0.4128	-	-	43.9
	$a_{T\text{ calc}}$	30.365	8.415	2.721	1	0.4091	-	0.0146	
	%error	0.3013	0.953	1.2865	0	0.8885	-	-	
PRic-10	a_T	21.48	5.387	2.294	1	0.4504	-	-	42.98
	$a_{T\text{ calc}}$	20.061	6.498	2.410	1	0.456	0.089	-	
	%error	6.608	20.62	5.045	0	1.243	-	-	

*: Reference temperature - $a_{T\text{ calc}}$ are shift factors from computation using Arrhenius law

REFERENCE

- 1 D. Van Krevelen and K. Nijenhuis, *Properties of Polymers*, Elsevier, 1992, vol. 16.