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

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Fig SI – 2: ^{1}H NMR spectra of polyricinoleate in CDCl$_3$
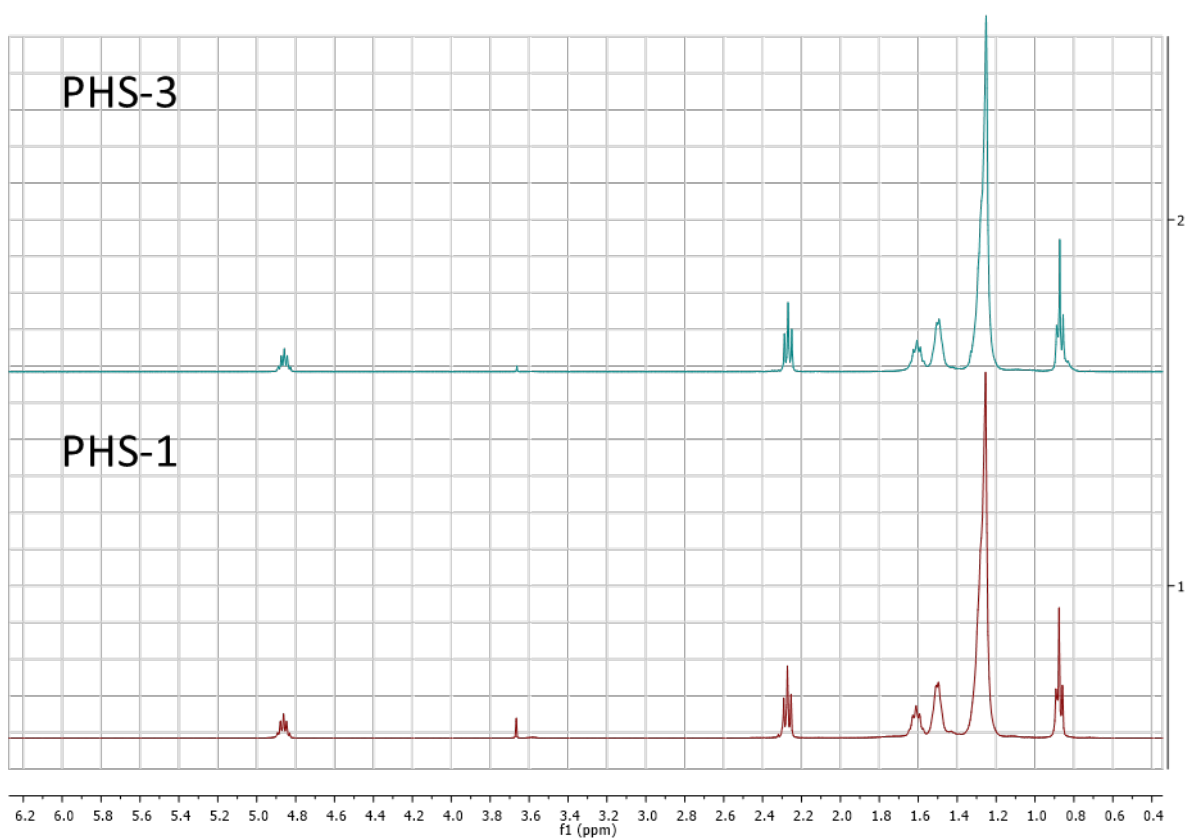
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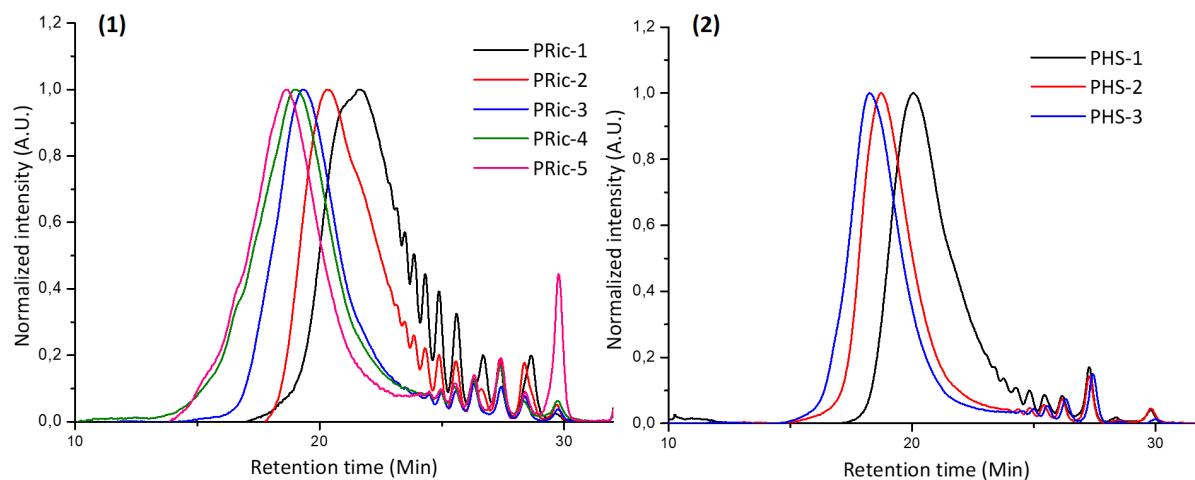
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<u>Rheometry analysis:</u>

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).

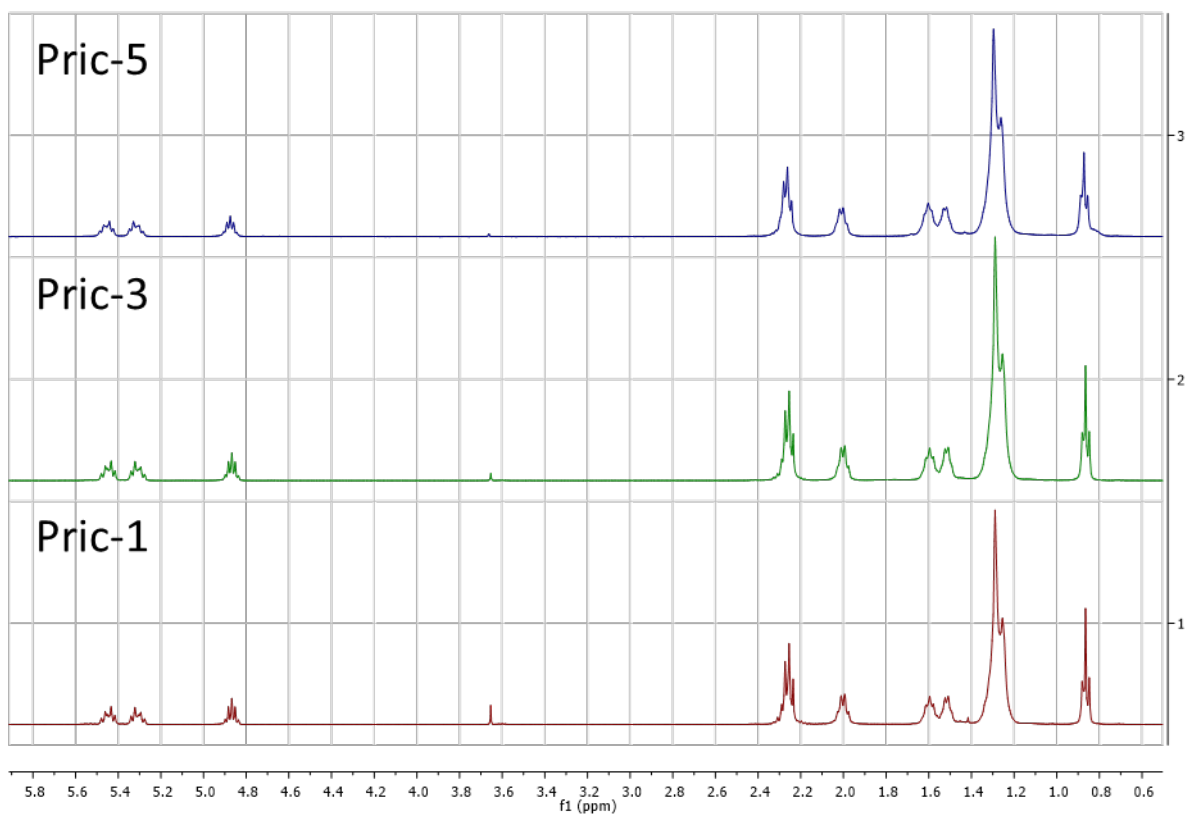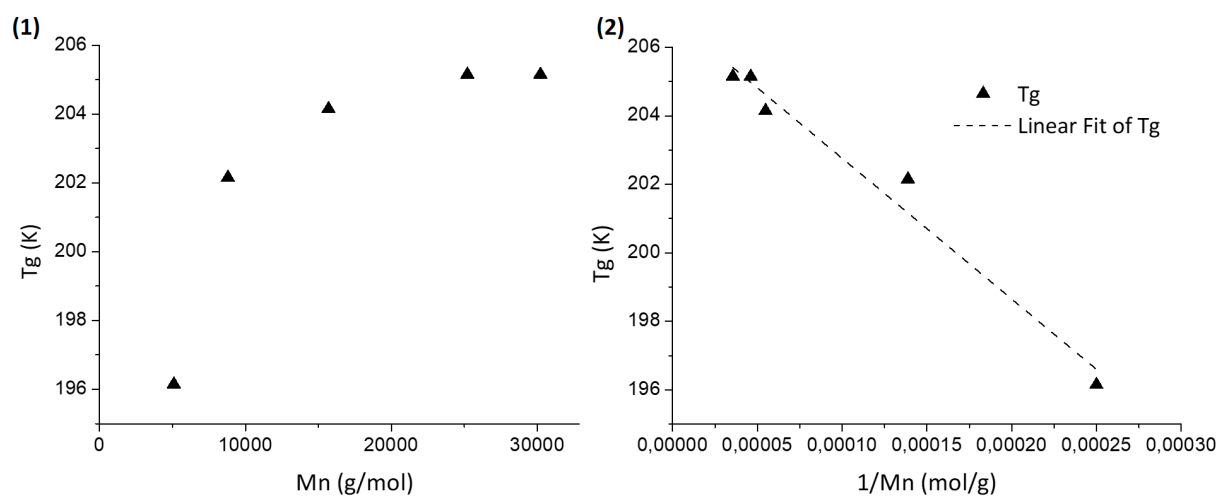The complex viscosity was calculated with the data obtained from the dynamic shear measurements according to equation 1.[1]

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

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 $a_{T/\text{Tref}}$ used to establish master curves follows an Andrade law[1] 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 Newtonianviscosities could be estimated at 20 °C for all the polymers..

$$y = 11292x - 44.65$$
$$R^2 = 0.999$$

$$y = 5976x - 23.67$$
$$R^2 = 0.994$$

$$y = 6804x - 26.93$$
$$R^2 = 0.999$$

$$y = 6599x - 26.1$$
$$R^2 = 0.997$$

$$y = 6428x - 25.45$$
$$R^2 = 0.999$$
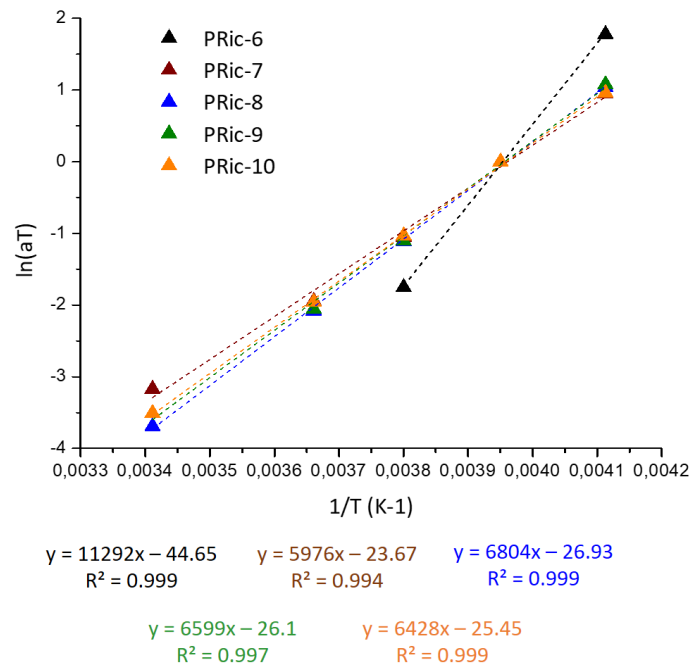
Figure SI - 6: Translation factor as a function of 1/T fitted with Andrade law

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 γ=1% was fixed for the frequency sweep experiments.
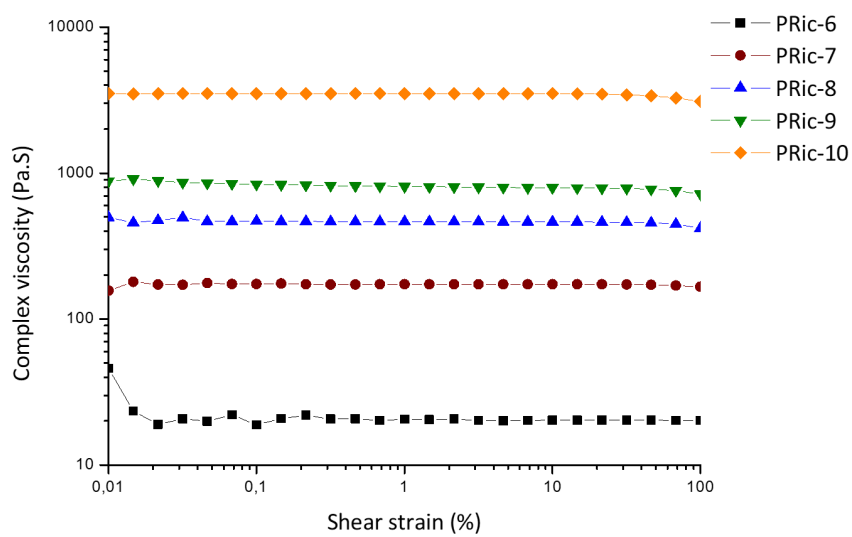
Figure SI - 7: Complex viscosity as a function of shear strain for a series of PRic with various M_w. Performed at 20°C with an angular frequency of 10 rad.s^{-1}

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 °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 $0{,}003 < \omega < 294$ rad.s^{-1} at -20 °C. Results are plotted in Figure SI-9.

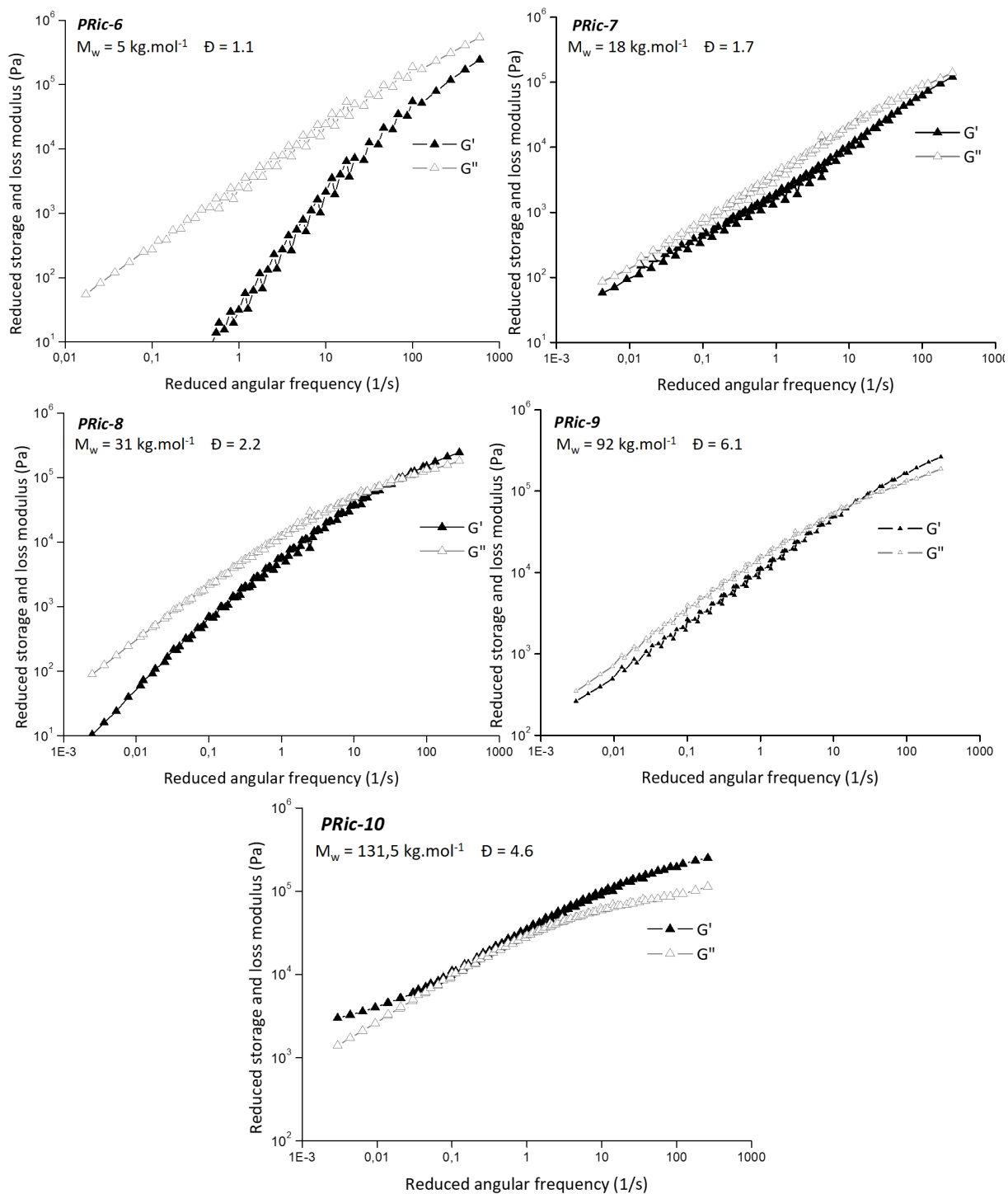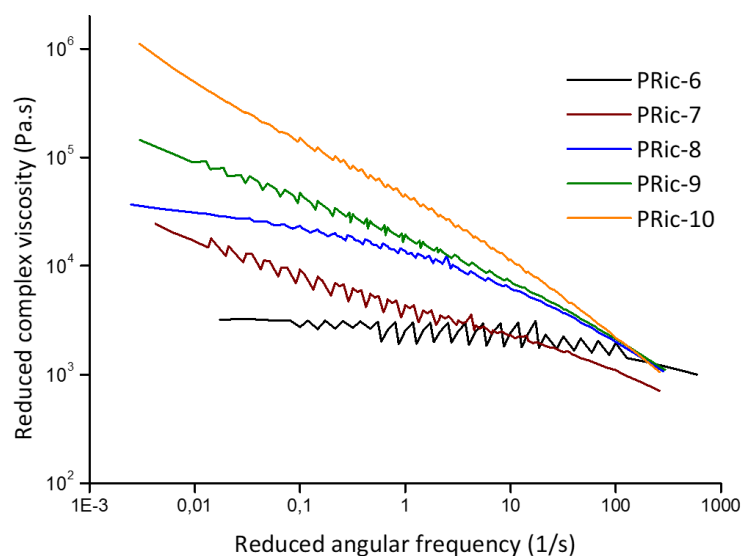Figure SI - 9: Polyricinoleate reduced complex viscosity versus the reduced angular frequency obtained from TTS at -20 °C as reference temperature, 1% shear strain

Regarding the master curves in Figure SI-8, it appears clearly that for most of the polyricinoleate 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 $\omega < 1$ rad.s^{-1} in the case of PRic-6 and $\omega < 0.1$ rad.s^{-1} in the case of PRic-8 allowing determination of a Newtonian viscosity at -20°C

PRic-6: $\eta^*_{-20\ °C}$= 3010 ± 230 Pa s

PRic-8: $\eta^*_{-20\ °C}$= 34900 ± 1500 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

PRic-7: $\eta_{20\ °C}$= 28.80 ± 0.03Pa.s

PRic-9: $\eta_{200\,°C}$= 124.8 ± 2.2 Pa.s

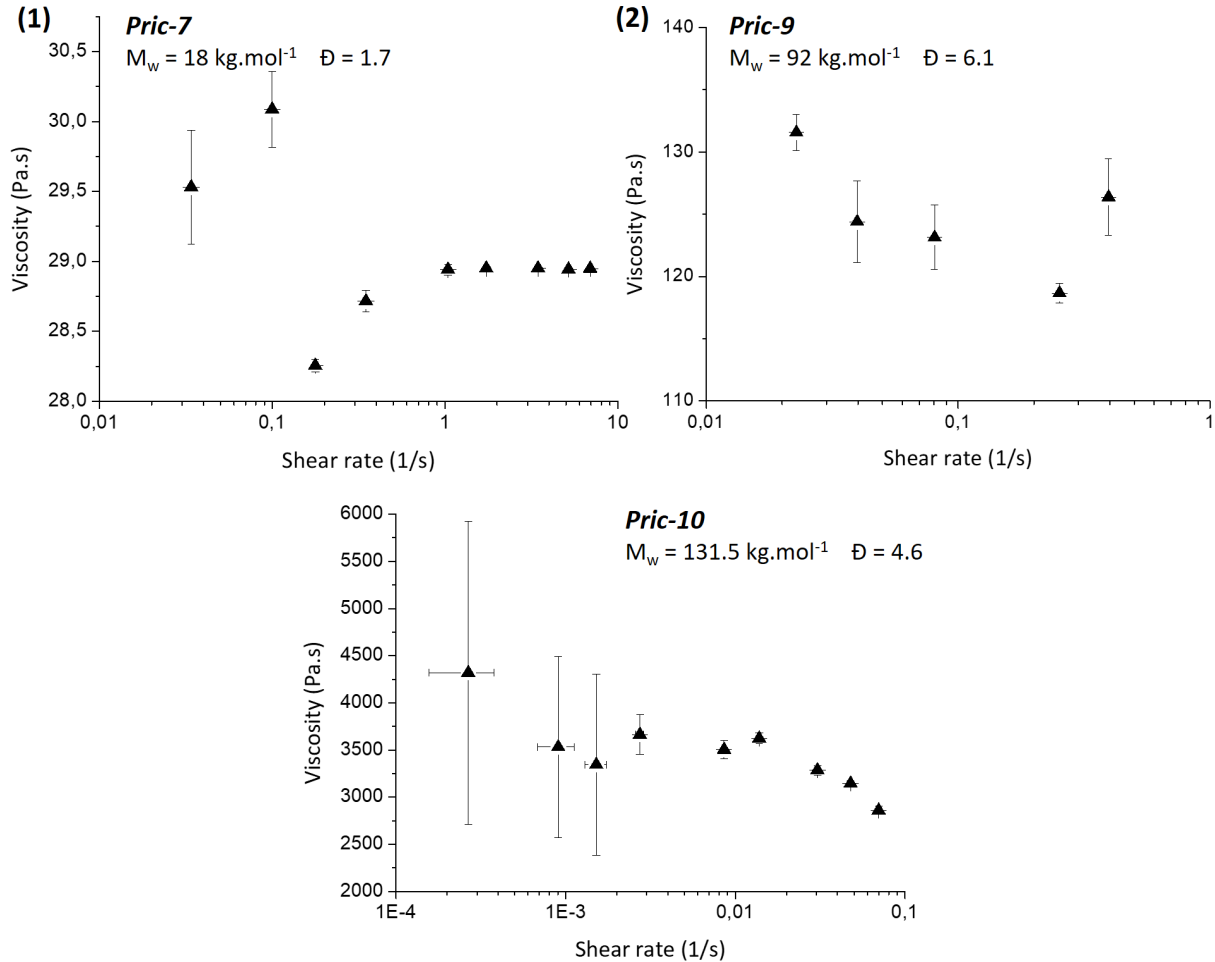PRic-10: $\eta_{150\,°C}$= 3500 ± 100 Pa.s

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(aTw) 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.
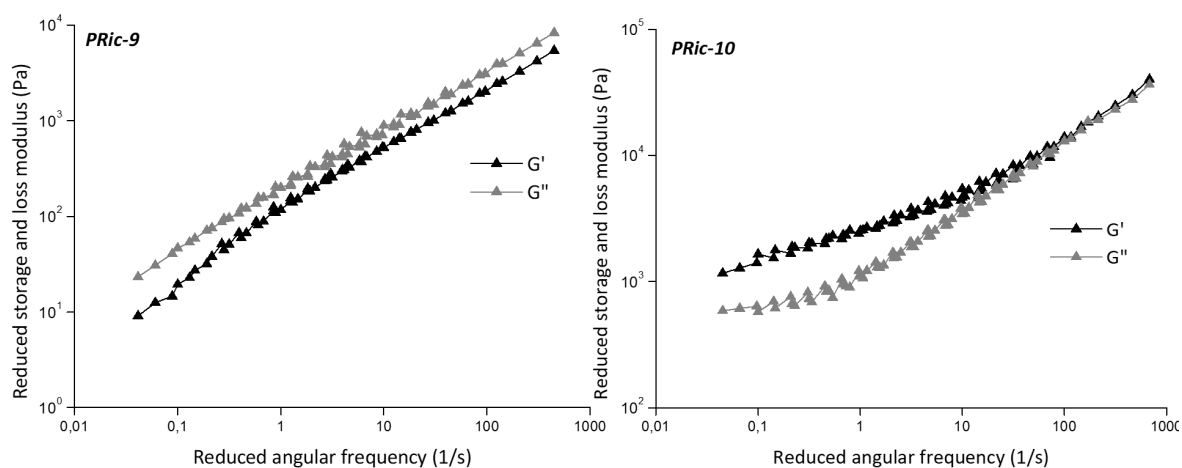

Figure SI-11: Master curves at 80°C of PRic-9 and PRic-10 samples. Reduced storage and loss modulus are expressed versus the reduced angular frequency

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

*: Reference temperature - $a_{T calc}$ 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	-	-	
	$a_{T\,calc}$	30.365	8.415	2.721	1	0.4091	-	0.0146	43.9
	%error	0.3013	0.953	1.2865	0	0.8885	-	-	
PRic-10	a_T	21.48	5.387	2.294	1	0.4504	-	-	
	$a_{T\,calc}$	20.061	6.498	2.410	1	0.456	0.089	-	42.98
	%error	6.608	20.62	5.045	0	1.243	-	-	

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

REFERENCE

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