

Entanglements and rheology of poly(4-methyl-1-pentene)

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Entanglements and Rheology of Poly(4-Methyl-1-Pentene)

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Introduction

P4M1P shows different physics when is compared with polymers like PE, PP and PS. Side groups (-C3H7, -CH3 and -C6H6) are expected to influence rheology, processing and crystallisation. Crystallisation rate follows the trend PE > P4M1P ≈ PP > PS; P4M1P presents a higher crystallisation rate than the expected for a polymer with a big side group. This could be linked to a “more disentangled” state of macromolecules. They are then free to arrange faster on cooling. Rheological techniques can help us to enlighten this question.

Experimental

Dynamic oscillatory measurements were undertaken on an ARES rheometer in a broad range of frequencies and temperatures above T_m (520 °K) for two P4M1P samples labelled as SP2 and SP5 differing in molecular weight (M). The experiments were conducted with test specimens moulded in a hot-press. The results have been compared with those of well-know polymeric materials as PE, PP and PS.

Results

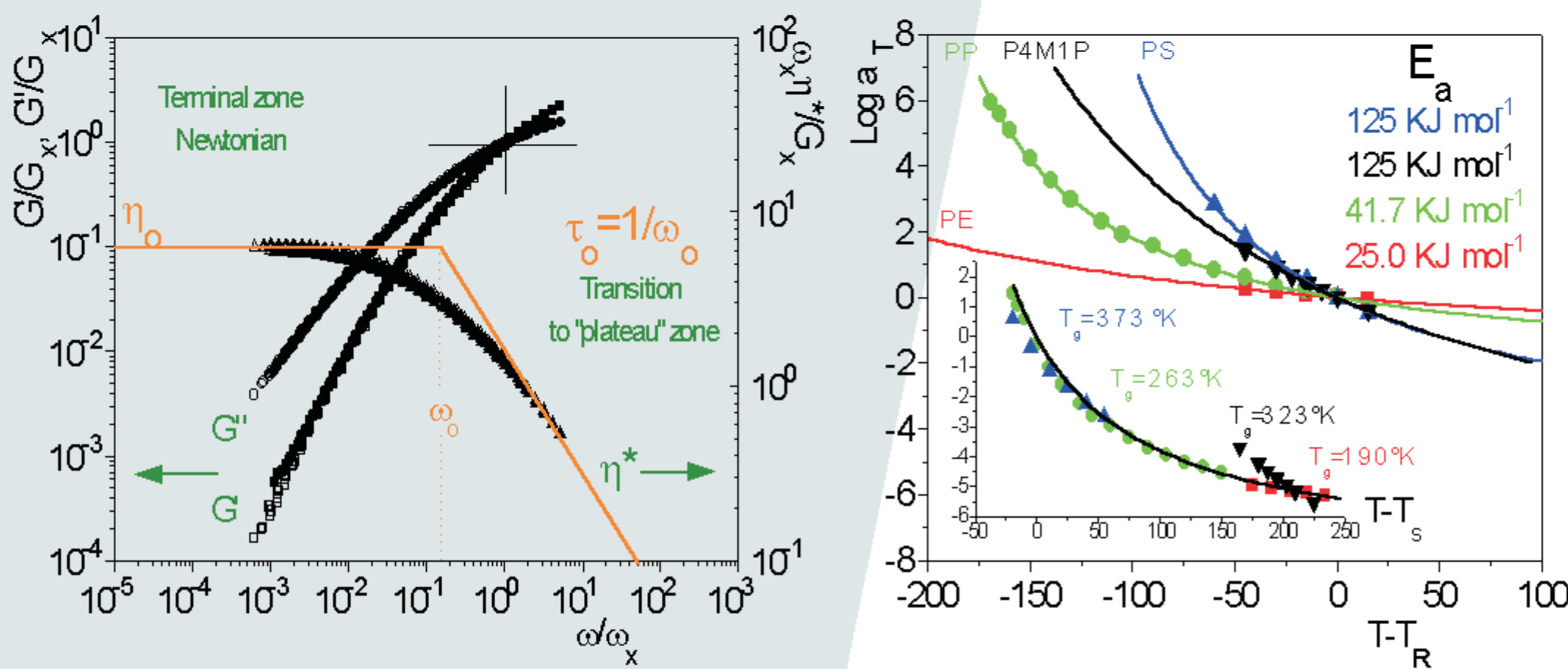


Figure 1 (left). Normalised linear viscoelastic fingerprint to the cross-point modulus co-ordinates (G_x and ω_x) for SP2 (open symbols) and SP5 (full symbols) samples. Figure 2 (right). Temperature dependence of viscoelastic properties expressed as the frequency shift factor a_T .

The samples show the expected behaviour of entangled polymeric systems (fig. 1). One can define the Newtonian viscosity (η_0) at very low frequencies and also a relaxation time for the onset of a transition at higher frequencies (τ_0) related to the reptation time, τ_d .

The temperature dependence is a function of the bulkiness of side groups: PE < PP < P4M1P ≈ PS (fig. 2). However, on testing the William-Landel-Ferry (WLF) master temperature dependence of viscoelastic properties at a constant distance from the glass transition temperature T_g , $T_s = T_g + 50$ ($C_1^s = 7.6$ and $C_2^s = 100^\circ K$) (1) it is found that P4M1P samples behave differently. This is not the only difference among the samples (see table below).

← Crystallisation rate

Material	PE	P4M1P	PP	PS
$T_g / ^\circ K$	193	323	263	373
$T_m / ^\circ K$	409	518	433	523
$T_m - T_g$	216	195	170	150

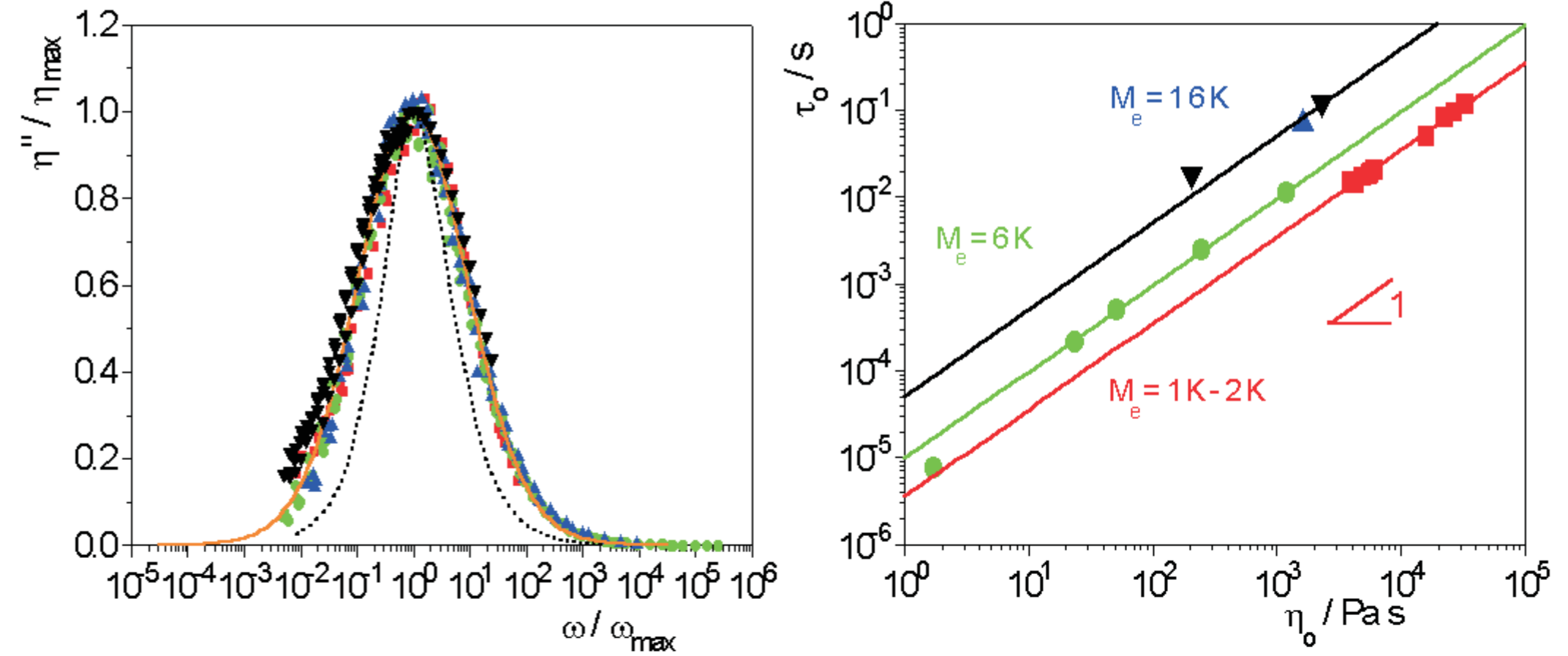
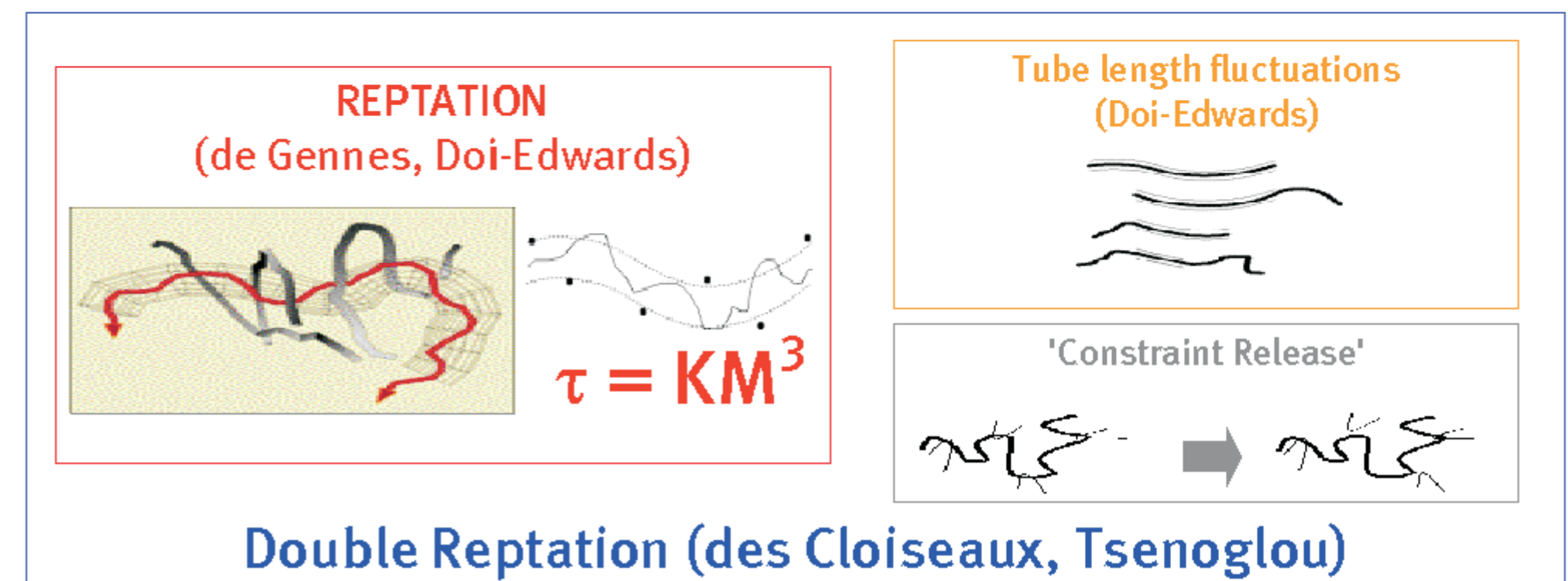


Figure 3 (left). Normalised out-of-phase component of η^* : (.....) monodisperse sample, (—) reptation model. Figure 4 (right). Relaxation time vs. Newtonian viscosity (1).

The relaxation spectrum of P4M1P is similar to that of materials with polydispersity index, $M_w/M_n = 2$ (2): the effect of M_w/M_n is avoided when one compares them (fig. 3 and 4). The dynamics of entangled melts has been tested by applying the double reptation model (3).

We know that: $\tau_d \propto \tau_0 \propto \eta_0(M)/G_N^0(M_e)$; G_N^0 is the “plateau” modulus and M_e the molecular weight between entanglements. At a given value of η_0 (eliminating the effect of M) is found that the higher τ_d , the higher M_e . The higher M_e values correspond to P4M1P and PS (fig. 4).



Conclusions

P4M1P shows the characteristic viscoelastic behaviour of an entangled polymer network. The dynamics can be modelled by the reptation model. Eliminating the effects of M and M_w/M_n , the dynamics of the P4M1P is similar to that of PS, thus P4M1P is at least as entangled as PS. The temperature dependence is in agreement with the bulkiness of the side group, but not with the behavior expected from WLF universal correlation. The clue for the higher crystallisation rates may be in the distance $T_m - T_g$ (or $T_c - T_g$, being T_c the crystallisation temperature). The higher the crystallisation rate the longer this distance: the dynamics of macromolecules goes faster far above T_g .

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