

Polymer Dynamics and Rheology in Designing and Understanding Polymeric Biomaterials for Tissue Engineering Applications

Shanfeng Wang, Lichun Lu, Michael J. Yaszemski

Mayo Clinic College of Medicine, Rochester, Minnesota 55905, USA

Polymer dynamics is the essence of polymer physics. Understanding polymers from the perspective of polymer dynamics is crucial to rationally design and fabricate novel polymeric systems. Poly(propylene fumarate) (PPF) and poly(propylene fumarate)-co-polycaprolactone (PPF-co-PCL) (Fig. 1) are two unsaturated linear polyesters that can be crosslinked through its fumarate double bonds.^{1,2} By varying the composition of PPF-co-PCL, controllable physical properties can be achieved to satisfy various needs in tissue engineering, particularly, bone and nerve regenerations.² Both molecular weight dependence and composition dependence of their physical properties are studied in detail using the tools of polymer dynamics and rheology. The aim of this work is not only to supply an extensive library of important properties of these polymers but also to bridge the gap between the polymer theory and practical applications.

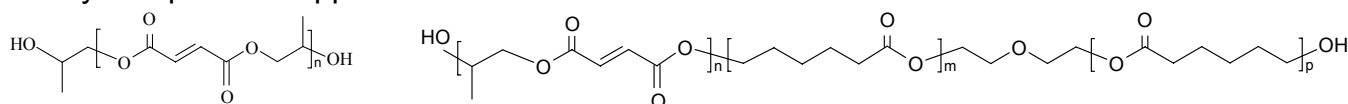


Figure 1. Chemical structures of PPF (left) and PPF-co-PCL (right).

The PPF samples synthesized directly from polycondensation³ have weight-average molecular weights (M_w) varying from 1.1 to 11 kg.mol⁻¹ and a polydispersity between 1.4 and 2.8. Ten relatively monodisperse (polydispersity: 1.21-1.78) fractions were obtained from fractionation. Fifteen PPF-co-PCL copolymers with various PCL weight compositions ranging from 29 to 90% were synthesized as described earlier and their M_w s are between 8.2 and 47.1 kg.mol⁻¹. PPF and PPF-co-PCL samples are named with their M_w and PCL composition in the latter discussion, respectively. Gel Permeation Chromatography (GPC) was performed with a Waters 717 Plus autosampler GPC system connected to a model 515 HPLC pump and model 2410 refractive index detector using monodisperse polystyrene standards. Differential Scanning Calorimetry (DSC) was done on a TA Instruments Q1000 differential scanning calorimeter at a heating rate of 10 °C/min under nitrogen. Linear viscoelastic properties of PPF samples are measured by a rheometer (AR2000, TA instruments) at frequencies ranging from 0.1 to 628.3 rad/s and at temperatures between 0 and 100 °C. Oscillatory shear measurements were carried out using a 20 mm diameter parallel plate flow cell with a geometry gap of 1.0 mm to measure the storage and loss moduli G' and G'' besides the zero-shear viscosity η_0 . A small strain ($\gamma < 0.05$) was always used when $|G^*|$ was large, and no strain amplitudes were greater than 0.10.

A small fraction of branching or partial crosslinking occurred due to Ordelt reaction,³ i.e., the addition of glycols onto the double bonds of unsaturated segments. New methods such as transesterification between diester of fumaric acids and diols and the use of less acidic catalyst $ZnCl_2$ have been invented to reduce the Ordelt reaction efficiently.³ Piras⁴ showed that the chain branches caused by Ordelt saturation are mostly monomer short-chain branches. Besides the short-chain branches, only a slight fraction (<3 wt.%) due to partial crosslinking can be found in the GPC curves of high molecular weight PPF. Therefore, the PPF and PPF-

co-PCL samples can be considered as linear chains. DSC results show that all the PPF samples are amorphous and there is a single glass transition. T_g increases dramatically with molecular weight from ~ -30 to ~ 30 °C when the molecular weight is lower than a critical M_n around 5000 g.mol^{-1} . For PPF-co-PCL, T_g decreases with increasing the PCL composition and crystalline structure appears in the copolymers with PCL composition higher than 70%.

Time-temperature superposition⁵ was applicable for all the polymers in the temperature range studied here and the master curves reduced to 40 or 25 °C were formed as shown in Fig. 2a. The master curves for PPF11.2K at 40 °C in Fig. 2a and PPF7.9K at 25 °C in Fig. 2b were not obtained directly but shifted horizontally from the information at higher temperatures instead. It can be seen from the master curves that almost all the copolymers and PPF samples are either unentangled or marginally entangled. In the terminal regime at low frequencies, typical relations in G' and G'' functions as $G' \sim \omega^2$ and $G'' \sim \omega^1$ can be observed.⁵ As usually expected for the terminal regime at lower frequencies, the glass regime at higher frequencies for different PPF samples also shifts to lower frequency region with increasing molecular weights. It implies that the local segmental motion in PPF varies with molecular weight in the molecular weight range studied here. For the unentangled systems here, their relaxation times can be estimated by using the positions of G' and G'' master curves. The relaxation time decreases dramatically as much as 4-5 decades through changing chain friction coefficient and flexibility after introducing PCL segments into PPF backbone, despite of higher copolymer molecular weights than PPF7.9K.

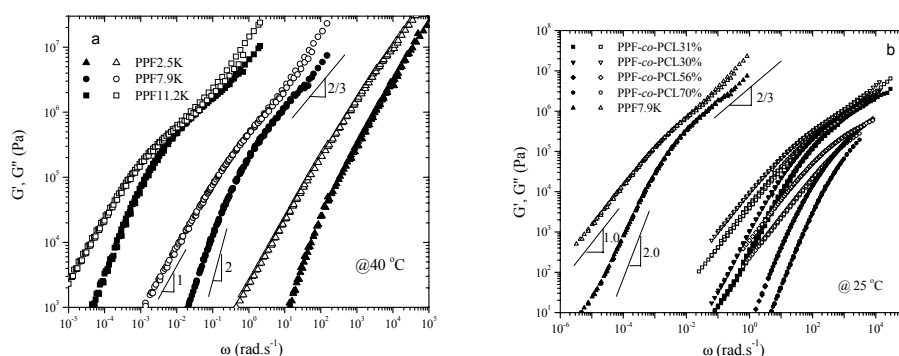


Figure 2. Master curves of G' (solid symbols) and G'' (open symbols): of (a) PPF with different molecular weights; (b) PPF7.9K and copolymers at the reference temperatures of 40 and 25 °C, respectively.

The temperature dependence of η_0 is shown in Fig. 3a. This temperature dependence varies with molecular weight. A smooth progression with molecular weight is evident in the inset of Fig. 3a when the viscosity data were normalized to the values at 40 °C. The temperature dependence for PPF7.9K with an M_w of 7910 g.mol^{-1} is the strongest and the viscosity varies as much as 4 orders of magnitude when the temperature changes from 40 to 100 °C. This phenomenon is another manifestation of the molecular weight dependence of T_g . The η_0 data in Fig. 3a are replotted in Fig. 3b, with the temperature subtracted by the corresponding T_g of each PPF. All the seven PPF samples share the same $(T-T_g)$ dependence. Furthermore, all the data can be well superposed together after vertical shifts by taking out the pure chain length effect on η_0 , shown in the inset of Fig. 3b.

The temperature dependence of η_0 for all the copolymers, PPF2.5K, and PCL2K is shown in Fig. 4a. The temperature dependence for η_0 varies with PCL composition. A smooth progression with increasing PCL composition in the copolymers is evident in the inset of Fig. 4a when viscosity data were normalized to the value at 40 °C. The temperature dependence for PPF2.5K is the strongest and the viscosity ranges over as much as 6 orders of magnitude when the temperature changes from 10 to 100 °C, while it is rather weak for PCL2K and other copolymers with high PCL compositions. The temperature dependences of η_0 in Fig. 4a can be replotted against $T-T_g$ or T_g/T in Figure 4b to reach iso-friction state approximately. In contrast with PPF in Fig. 3, the changing temperature-dependence of η_0 with the PCL composition still exists in Fig. 4b. Due to the chemical structure of PPF, higher fragility for copolymers with higher PPF composition is implied from the inset of Fig. 4b.

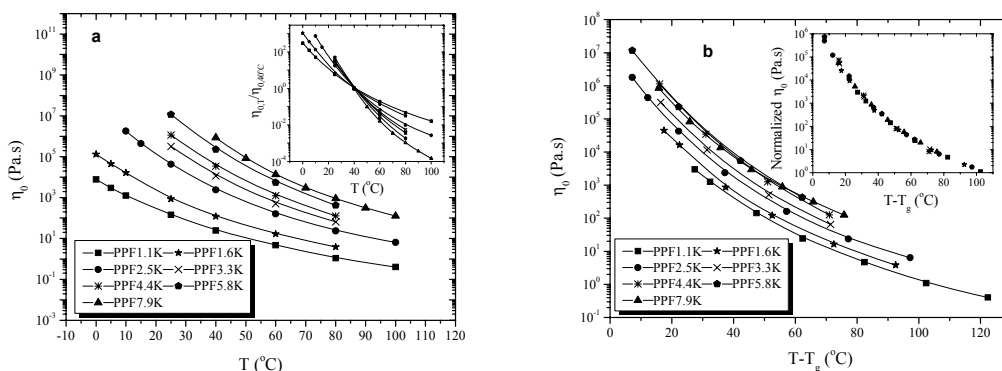


Figure 3. PPF melt viscosity vs. (a) T and (b) $T-T_g$. Inset in (a): viscosities at various temperatures reduced to 40 °C vs. T . Inset in (b): viscosities at various temperatures vertically shifted to the data for PPF1.1K vs. $T-T_g$.

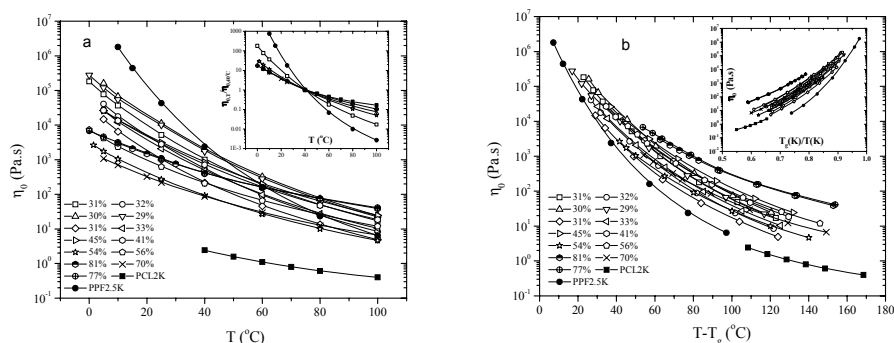


Figure 4. Viscosities versus (a) T , (b) $T-T_g$, and inset of (b) T_g/T for PPF2.5K, PCL2K, and copolymers shown as PCL compositions. Inset in (a): normalized viscosity to the temperature of 40 °C vs. temperature for PPF2.5K, copolymers, and PCL2K.

For unentangled and entangled polymers, it is well known that the molecular weight dependence for melt viscosity can be described as $\eta_0 \sim M^{1.0}$ using Rouse model and $\eta_0 \sim M^{3.0}$ using reptation model, respectively.⁵ Since both Rouse model and reptation model are single chain approaches, they have been modified to interpret the stronger molecular weight

dependences in polymer melts.⁵ Fig. 5 shows the molecular weight dependence of the viscosity for PPF and six copolymers with a similar PCL composition of ~30% at various temperatures. The linearity in Fig. 5b suggests the microstructure such as block length and distribution does not influence the macroscopical property η_0 strongly, as long as the block composition is fixed. The exponent a in $\eta_0 \sim M^a$ decreases from 7.0 for PPF and 2.24 for PPF-co-PCL at 25 °C to 3.1 for PPF and 1.47 for PPF-co-PCL at 100 °C, indicating the unentangled characteristics and the weakened free volume effect at higher temperatures. Rouse prediction can be satisfactorily approached for PPF and copolymers after iso-friction correction by measuring the viscosity at the temperature with the same distance from the PPF and copolymers' T_g , respectively.

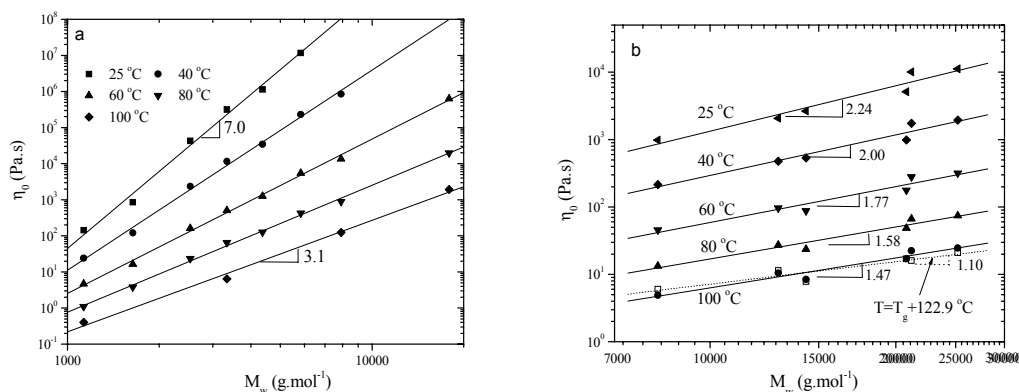


Figure 5. Molecular weight dependence of η_0 at various temperatures for (a) PPF and (b) copolymers with PCL composition of ~30%.

In conclusion, PPF and PPF-co-PCL have been investigated using polymer dynamics and rheology. Both terminal and segmental relaxations as well as η_0 and T_g show a very significant finite length effect in the molecular weight range studied here. The temperature dependence of viscosity for PPF with various molecular weights can be unified when the temperature is normalized to T_g . Although the copolymer molecular weights are higher than that of PPF, the relaxation of PPF-co-PCL copolymers is much faster and T_g is much lower than that of PPF. Due to the chemical structure of PPF, higher fragilities have been revealed for the copolymers with higher PPF compositions.

References

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Acknowledgments

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