Manipulation of Molecular Weight Distribution Shape as a New Strategy to Control Processing Parameters

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Molecular weight and dispersity ($Đ$) influence physical and rheological properties of polymers, which are of significant importance in polymer processing technologies. However, these parameters provide only partial information about the precise composition of polymers, which is reflected by the shape and symmetry of molecular weight distribution (MWD). In this work, the effect of MWD symmetry on thermal and rheological properties of polymers with identical molecular weights and $Đ$ is demonstrated. Remarkably, when the MWD is skewed to higher molecular weight, a higher glass transition temperature (T_g), increased stiffness, increased thermal stability, and higher apparent viscosities are observed. These observed differences are attributed to the chain length composition of the polymers, easily controlled by the synthetic strategy. This work demonstrates a versatile approach to engineer the properties of polymers using controlled synthesis to skew the shape of MWD.

1. Introduction

Understanding the thermal and viscoelastic properties of polymers is critical for the engineering and determination of processing conditions in important industrial technologies, such as hot-melt extrusion (HME), injection molding, and 3D printing (3DP).[1–4] It is well known that rheological properties of polymers are strongly influenced by their chemical structure, molecular weight, and polydispersity ($Đ$).[2,5–10] In particular, variations in $Đ$ change the relaxation profiles of polymers by shifting their crossover point, and affect the range of deformation rates and temperatures required for melt processing.[2,5] However, $Đ$ provides only partial information about the relative distribution of polymer chain sizes, being defined as a ratio of the weight-average (M_w) and the number-average (M_n) molecular weights.

Therefore, $Đ$ does not provide information about the symmetry and shape of molecular weight distribution (MWD), which also influences polymer properties.[11,12] Previous studies on MWD effects on polymer properties have been limited in their rigor due to insufficient technology to precisely control the shape and symmetry of the distribution. A simple approach to tuning polymer processability without changing its chemical characteristics is highly desirable.

Recently, we developed a synthetic strategy to control the MWD shape of polymers with identical M_n and $Đ$ by feeding the initiation species into a controlled polymerization process at predetermined rates and times. This temporal control of chain initiation dictates the molar quantities of each chain length in the final material.[11,12] This simple and scalable synthetic method to control the symmetry (skewness) of MWDs enables the next generation of structure property investigations. Of particular interest is the effect of molecular composition, or skewness of the distribution, on the rheological properties of polymers. This modular approach enables the preparation of polymers with complementary (opposite) skewness, and therefore enables the extension of systematic investigations of the classical effects of M_n and $Đ$ on rheological properties of polymers.

In this work, we investigate and compare thermal and rheological properties of linear polymers with identical M_n and $Đ$, but with distinctly different skewness of MWDs. We demonstrate that a facile synthetic technique to control the symmetry of MWD enables the tuning of thermal and rheological properties of polymers towards desired performances, such as enhanced thermal stability or lowered processing temperatures.

2. Experimental Section

2.1. Anionic Polymerization of Skewed Polystyrenes (PS$_{LOW}$, PS$_{HIGH}$)

All reactions were performed in a UnilabMBraunGlovebox. Styrene (99%, Sigma Aldrich) was stirred over calcium hydride (CaH$_2$) overnight and vacuum transferred into a flame dried Schlenk bomb followed by three freeze–pump–thaw cycles. Cyclohexane (Fisher Scientific, ACS Grade) was distilled under

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argon after stirring over a 1:1 mixture of *sec*-butyllithium (*s*-BuLi) and diphenylethylene (deep red) for 1 h followed by three freeze–pump–thaw cycles. *s*-BuLi (1.4 M, Sigma Aldrich) and isopropanol (Sigma Aldrich) were used as received. Polystyrene samples PS_{HIGH} and PS_{LOW} were synthesized by previously described procedure.[11,12] Briefly, PS_{HIGH} was prepared by slow addition of *s*-BuLi (516 µL, 35×10^{-3} M) at constant rate of 516 µL h^{-1} to a solution of styrene (1 mL) in cyclohexane (8 mL). PS_{LOW} was prepared in a similar manner with an exponentially ramped addition rate of *s*-BuLi over 2.5 h. Each reaction was quenched with a few drops of isopropanol after 6 h. These polymers were isolated by removing the solvent under reduced pressure to yield a white solid.

2.2. Size Exclusion Chromatography (SEC)

All polymer MWDs were characterized using a Tosoh EcoSEC HLC 8320GPC system with two SuperHM-M columns in series and a flow rate of 0.350 mL min^{-1} with tetrahydrofuran as the eluent. Number-average molecular weights, weight-average molecular weights, dispersities, and asymmetry factors, were calculated from refractive index chromatograms against TSKgel polystyrene standards.

2.3. Rheological Measurements

Rheological characterization was conducted on a controlled stress rheometer with parallel plates geometry (40 mm diameter, AR-G2, TA Instruments). For all the rheological tests, solid samples were used by compressing and melting polystyrene powder into 40 mm diameter uniform slabs.[1] Dynamic mechanical analysis (DMA) was performed by ramping up the temperature at constant increments of 3 °C from 50 to 160 °C, at a constant angular frequency of 6.283 rad s^{-1} and 0.5% strain. Apparent viscosity measurements were conducted by a continuous ramp up of the shear rate from 0.1 to 1000 s^{-1} at a constant temperature (25 and 150 °C). Frequency sweep tests were performed by scanning angular frequencies from 0.1 to 628.3 rad s^{-1} under 1.0% strain at various temperatures (25, 120, and 150 °C). The rheological measurements were repeated ($n = 3$) to assure reproducibility.

2.4. Thermogravimetric Analysis (TGA)

The analysis was performed on a PerkinElmer Diamond instrument (Pyris Diamond TG-DTA, High Temp 115). The sample was placed in an alumina crucible and heated from 30 to 600 °C at a constant rate of 10 °C min^{-1} under nitrogen flow. The degradation temperature was indicated as a transition point where the sharpest change in the curve occurred (a point of a drastic change in the slope). The measurements were repeated ($n = 3$) to assure reproducibility.

2.5. Differential Scanning Calorimetry (DSC)

The tests were conducted on a PerkinElmer DSC8500, with a scanning rate of 10 °C min^{-1}, in the temperature range of 25–200 °C.

3. Results and Discussion

Two different linear polystyrene samples were prepared by a previously reported method demonstrated in **Figure 1**a (initiation profiles are shown in Figure S1 of the Supporting Information).[11] The M_n and M_w of the synthesized polymers were identical (73.5 and 101.4 kDa, respectively, $Đ = 1.38$), as indicated by SEC. However, the MWD skew of these polymers was opposite. Asymmetry factor (A_s) was used as a relative measure of sample skewness and is defined as the distance of the center line (peak max) to the back slope divided by the center line to the front slope at 10% peak height.[11–13] One sample with a positive skew (PS_{HIGH}, high molecular weight skew, $A_s = 1.8$) and one with a negative skew (PS_{LOW}, low molecular weight skew, $A_s = 0.4$) were synthesized.[11] The distinctly different MWD symmetries are evident by SEC traces shown in Figure 1b.

The glass transition temperature (T_g) is a fundamental and critical parameter to investigate in any polymer system. Below the T_g, the stiffness of polymers, associated with their dominant solid-like nature, limits their ability to disentangle and flow.[1,2] Therefore, the tan delta characteristic is crucial, as it determines the lowest temperature for an efficient melt processing. The effect of M_n and $Đ$ on T_g is well known,[1,9,10] however the effect of skewness has yet to be explored. DMA results
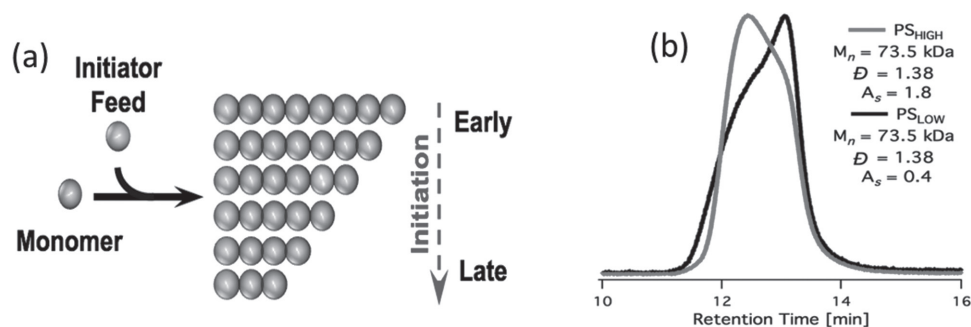

Figure 1. Preparation and characterization of polymers with skewed MWD. a) General strategy for controlling MWD shape through temporally regulating polymer chain initiation. b) SEC traces of polymers PS_{HIGH} and PS_{LOW}, which exhibit a distinctly different skewness of their MWD. Regardless of identical M_n and $Đ$, PS_{LOW} contains a larger fraction of low molecular weight polymer chains, and PS_{HIGH} has a higher fraction of high molecular weight polymer chains.
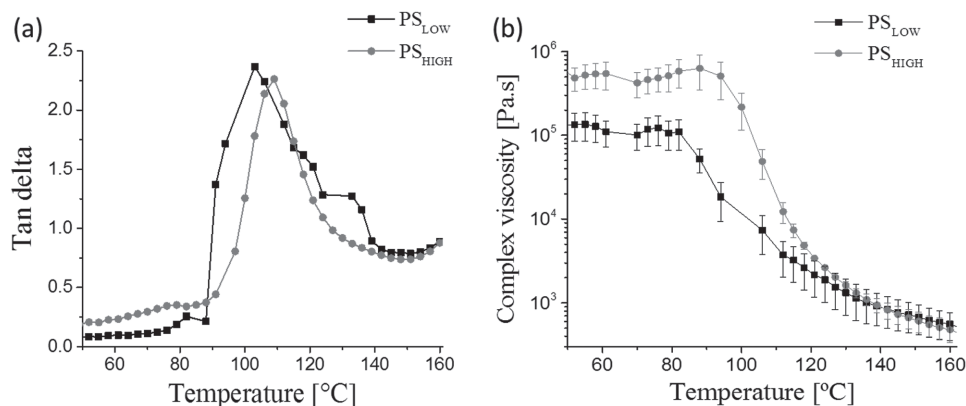
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Figure 2. Evaluation of temperature-dependent flow characteristics of PS_{HIGH} and PS_{LOW}. a) A representative tan delta curve demonstrates differences between the T_gs of PS_{HIGH} and PS_{LOW}. b) Complex viscosities of PS_{HIGH} and PS_{LOW} illustrate significantly higher stiffness of PS_{HIGH} in low temperatures region.

indicate noticeable differences between T_g values of PS_{LOW} and PS_{HIGH}, with the average values of 104.0 and 110.6 °C for PS_{LOW} and PS_{HIGH}, respectively. A representative loss tangent curve is demonstrated in **Figure 2**a (statistical data is shown in Figure S2 of the Supporting Information). The results are also supported by DSC (Figure S3, Supporting Information). The differences between the T_g values obtained by both methods can be attributed to the differences between the methodologies. While much larger amounts of polymer are used for DMA (gram scale); only a few milligrams of materials are used for DSC. Therefore, DMA provides a higher accuracy by taking into consideration mass attributions.[1] These differences are attributed to the variation in chain length composition of these polymers. Since shorter polymer chains require less thermal energy to disentangle and flow, the increase in their relative content decreases the transition temperature. These differences clearly demonstrate the effect of MWD symmetry on flow properties. Therefore, the ability to skew the symmetry of polymers by choosing the precise synthetic methodology,[11,12] gives direct control over the operating temperatures available for the melt processing of a specific polymer.

Viscosity is another essential property to be considered, which describes the dynamic response of viscoelastic materials to subjected temperatures and shears.[1] Viscosity profiles are crucial for polymer processing, since exceedingly high viscosities generate high torques during HME, and as a result may resist or even prevent the rotation of the screw.[1,2] When the viscosity is exceedingly low, extruded filaments fail to retain their desired shape.[2] Therefore, it is essential to establish a well-defined operational window for melt processability. Complex viscosity of PS_{HIGH} is significantly higher than that of PS_{LOW} between 50 and 127 °C (Figure 2b). With the increase in temperature, the complex viscosity of polymers PS_{LOW} and PS_{HIGH} gradually decreases as expected, and when the examined temperatures exceed 127 °C, the viscosity profiles of both polymers overlap and reach almost identical values. These observations can be attributed to the thermal relaxation achieved by polymers of different chain lengths at different temperatures. Above a critical temperature, all polymer compositions become sufficiently fluidic, exhibiting similar flow characteristics.

The optimal complex viscosity range for polymers used in HME has been previously reported as ≈1000–10,000 Pa s.[1,2] Adjusting the HME temperature accordingly allows a facile scalability of the process.[1] Therefore, these values define the recommended operational window for HME. While PS_{LOW} reaches optimal complex viscosity values between 106 and 138 °C, the optimal operational window of PS_{HIGH} requires elevated temperatures of 115–138 °C. As a result, the temperature range required for processing of PS_{LOW} is significantly broadened. Although both polymer samples exhibit identical M_n and Đ, differences in their molar mass compositions affect their processing temperature regime.

The examination of apparent viscosity indicates that both polymers exhibit shear thinning with almost identical shear thinning rates. However, both below and above the T_g PS_{HIGH} has a higher apparent viscosity. We demonstrate this at 25 and 150 °C, **Figure 3**a,b, respectively. At 25 °C, the apparent viscosity of PS_{HIGH} is ≈3 times higher than the apparent viscosity of PS_{LOW}. Significant differences are more obvious at the low shear region, but become less pronounced when shear rates reach ≈1000 s^{-1} (Figure 3a). Surprisingly, upon the increase in temperature to 150 °C, which is well above the T_g of both polymer samples, differences between the apparent viscosities were still observed (Figure 3b). The apparent viscosity of PS_{HIGH} remained 2–3 times higher than the apparent viscosity of PS_{LOW}. With the increase in shear rates above 300 s^{-1}, apparent viscosity profiles of both polymers became similar.

These findings indicate that even well above the T_g, where both short and long chain polymers are provided with sufficient energy to flow, chain length composition continues to contribute to physical properties. The ability to process polymers at decreased shear rates by implementing a simple synthetic approach can be harnessed to enhance the processability of polymers, especially when the availability of powerful high shear equipment is limited.

Macromolecular responses to stress and strain are time dependent, owing to the viscoelastic nature of the material at study.[2] To obtain an insight into the stiffness of PS_{HIGH} and $PS_{LOW,}$ dynamic moduli and complex viscosity were examined at 25, 120, and 150 °C (**Figure 4**). For all the examined temperatures, the storage modulus and the complex viscosity
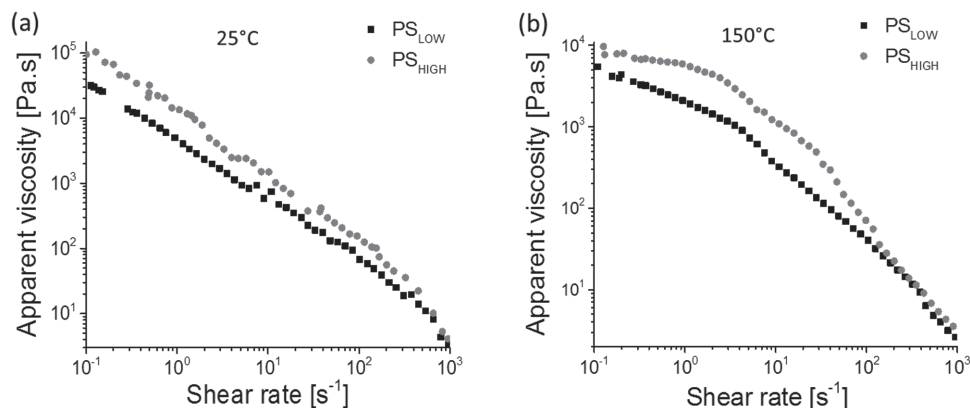
Figure 3. Apparent viscosity of polymers PS$_{HIGH}$ and PS$_{LOW}$ as a function of shear rate at a) 25 °C and b) 150 °C. The apparent viscosity of PS$_{HIGH}$ is higher than the apparent viscosity of PS$_{LOW}$.

of PS$_{HIGH}$ were consistently higher than those of PS$_{LOW}$, indicating its increased stiffness. The complex viscosities of PS$_{HIGH}$ and PS$_{LOW}$ gradually decreased with the increase in frequencies, as expected, for all the examined temperatures. At 25 °C storage moduli of both PS$_{HIGH}$ and PS$_{LOW}$ exhibited very weak frequency dependence, which can be attributed to their exceedingly dominant solid-like nature at room temperature within

the examined frequencies range (Figure 4a).With further increase in temperature above the T_g (120 and 150 °C), storage moduli decreased and exhibited strong frequency-dependent behavior. At 120 °C and high frequencies region, the storage modulus of PS$_{HIGH}$ was higher by almost one order of magnitude than the storage modulus of PS$_{LOW}$. Despite the reduction in the observed differences between PS$_{HIGH}$ and PS$_{LOW}$ moduli
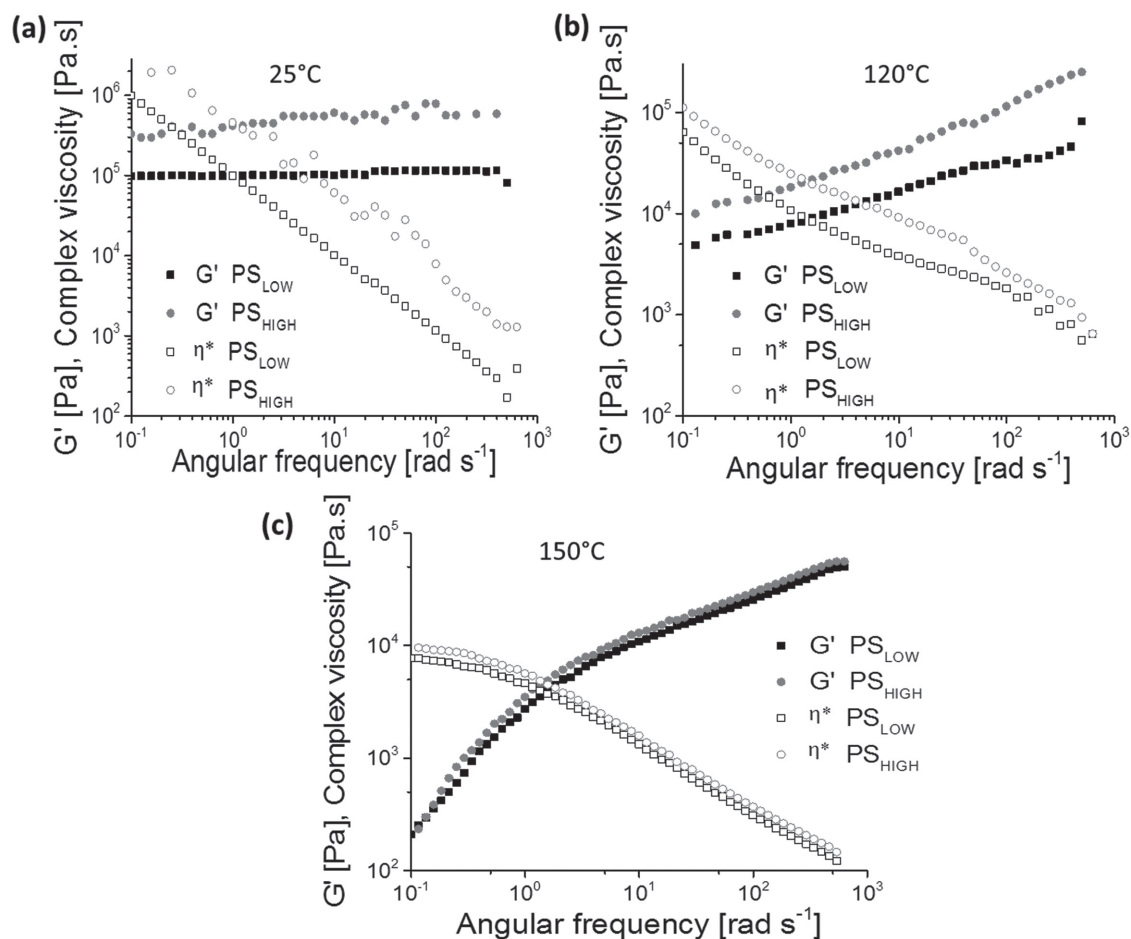

Figure 4. PS$_{HIGH}$ and PS$_{LOW}$ storage modulus and complex viscosity as a function of frequency at a) 25 °C, b) 120 °C, and c) 150 °C. PS$_{HIGH}$ storage modulus and complex viscosity are consistently higher than PS$_{LOW}$.

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at the low frequencies region, the storage modulus of PS$_{HIGH}$ remained up to 2 times higher than the storage modulus of PS$_{LOW}$ (see Figure 4b for representative data and Figure S4 of the Supporting Information for statistical data). The observed differences are attributed to the different chain length compositions of the polymers. PS$_{HIGH}$ contains a larger fraction of high molecular weight polymers than PS$_{LOW}$; therefore its response to the induced oscillatory deformation at shorter time scales is more limited, which is associated with a strong elastic response, represented by high storage modulus values. Although a similar trend is observed at the low frequencies region, with the gradual increase in provided relaxation time the effect of the molecular weight composition decreases, indicating less pronounced long term differences between the polymers. When the temperature increased to 150 °C, only small differences between the storage moduli and complex viscosities of PS$_{HIGH}$ and PS$_{LOW}$ were observed, which can be explained by sufficiently high energy provided to all polymer chain length compositions (Figure 4c). Frequency sweep results indicate that polymer stiffness is affected by polymer chain length composition, which was tuned by controlling the shape of MWD.

Another important characteristic for consideration during HME is thermal degradation temperature (T_d), which should not be exceeded during thermal processing of polymers in order to retain their function.[1] TGA shows differences between T_d values of PS$_{HIGH}$ and PS$_{LOW}$, demonstrated in Figure S5 (Supporting Information). The clearly observed differences in T_d (≈10 °C) and the degradation profiles of PS$_{HIGH}$ and PS$_{LOW}$ could be attributed to the different compositions of these polymers. The larger fraction of long chain polymers results in an improved thermal stability, which shifts the T_d to higher temperatures.[14]

Rheological differences between PS$_{HIGH}$ and PS$_{LOW}$ can be explained by the well-known reptation theory.[15] In the melted state, polymer chains are closely packed and their random motion is constrained by the neighboring chains. In the entangled systems the relaxation time of polymers is a function of the number of monomer units, reflected by their molecular weight, and strongly affecting their rheological properties. With the increase in molecular weight the number of entanglements increases, which reduces the mobility of polymer chains.[15] Therefore, skewing the MWD of polymers toward higher or lower molecular weights has a direct effect on their relaxation ability, providing a precise control over their rheological properties.

4. Conclusions

In summary, we have demonstrated that molecular composition of polymers, reflected by the shape and the symmetry of MWD, has a significant impact on their thermal and rheological properties. While the effect of M_n and $Đ$ on polymer processability has been broadly explored, these parameters provide only partial description of polymers viscoelastic and thermal properties. Shifting the symmetry of MWD toward a larger content of short chain polymers enables an efficient reduction of temperatures and shear rates required for polymer processing, which allows milder processing conditions and a broader operational window. When improved thermal stability is a major consideration, MWD symmetry shift toward a larger content of long chain polymers is favorable. We have demonstrated that MWD shape can serve as a powerful tool for the optimization of polymer processing parameters.

Conflict of Interest

The authors declare no conflict of interest.

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