

The viscoelastic behavior of polymer/oligomer blends

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ABSTRACT

The viscoelastic properties of poly(α -methyl styrene), its hexamer, and their athermal blends at various concentrations are studied. Master curves for the dynamic shear responses, G' and G'' , are successfully constructed for both the pure materials and the blends, indicating the validity of the time–temperature superposition principle for these systems. The temperature dependence of the shift factor follows the Vogel–Fulcher behavior over the temperature range studied, and the temperature dependence is slightly weaker for the blends. The rubbery plateau modulus scales with the polymer concentration as $G_N^0 \propto \phi^{2.04 \pm 0.32}$; the terminal relaxation time scales with the polymer concentration as $\tau_d \propto \phi^{1.35 \pm 0.33}$. The shape of the segmental dispersion appears unchanged by concentration, which differs from our calorimetric studies where mixtures show obviously temperature-broadened glass transitions and depressed enthalpy overshoots. The TNM (Tool–Narayanaswamy–Moynihan) model indicates that the change in the temperature dependence is not sufficient to account for the observed calorimetric broadening. We conclude that the temperature broadening of the glass transition for our blends is not due to a broadening of the dynamic spectrum or to changes in its temperature dependence. The possibility that the broadening is due to changes in the non-linearity parameter x in the TNM model is also considered. While the broadening could be due to a decreasing value of x , we found that this same decrease would lead to increasing enthalpy overshoots on heating, contrary to the experimental observations. The combination of the calorimetric results with the rheological measurements further indicates that the fundamental basis of the TNM-type of model of structural kinetics in glasses is potentially wrong.

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1. Introduction

Viscoelastic properties of miscible polymer blends or solutions have been extensively studied by a number of groups [1–21]. However, much of the work has focused on the terminal behavior or the transition to terminal region in efforts to test reptation or tube theories and entanglement effects on the rheological properties [1–13,15,17–22]; glassy dynamics of miscible blends have been rarely measured [14,16,23,24]. On the other hand, the glassy response of miscible blends has been well investigated using other techniques such as differential scanning calorimetry (DSC) [25–30], dielectric spectroscopy [27–31], and nuclear magnetic spectroscopy [32,33]. One of the prominent and interesting observations in these studies is a broadened glass transition (T_g) upon mixing. The broadening in T_g has been related to an increased heterogeneity, resulting from either concentration fluctuations [34–36] or chain connectivity effects [37–39]. Although much effort has been made to understand the

segmental dynamics and the heterogeneity in miscible blends, the origin of the broadened T_g is still not fully understood.

In two earlier publications from our laboratory [25,26], the glass transition behavior of binary blends of poly(α -methyl styrene) and its oligomers was investigated using DSC. The absolute glassy and liquid heat capacities were found to be functions of temperature but independent of blend composition, indicating that the mixtures are athermal. Upon blending, the calorimetric glass transition, i.e., the α relaxation, broadens (see Fig. 1), consistent with other studies on polymer/polymer blends using DSC [27–30], dielectric spectroscopy [27–32], quasielastic neutron scattering [32], and nuclear magnetic resonance (NMR) [32,33]. The calorimetric transition was partitioned to obtain the effective T_g s for each component of the blend, and the dependences of these effective T_g s on overall blend composition could be described by the Lodge–McLeish model, but the self-concentration effects were found to be extremely weak [26]. Considering that mixing a long chain polymer with a short chain oligomer would also suppress the concentration fluctuations of the system [35], neither the concentration fluctuations nor the chain connectivity effects seem likely to be responsible for the broadening in T_g .

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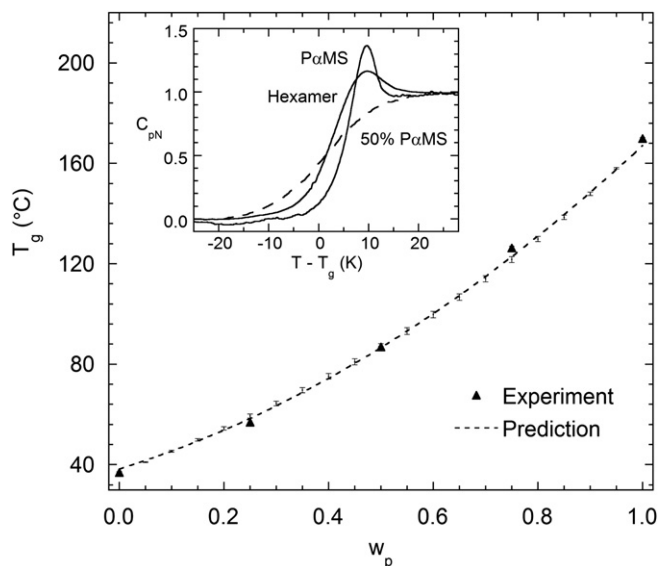


Fig. 1. T_g of the polymer (PαMS), the hexamer, and their blends plotted as a function of polymer weight percent. Dashed line is the prediction from the Pinal's [51] equation. Standard deviations on the experimental T_g and the prediction are also shown. Normalized heat capacities, C_{pN} , obtained on heating are shown in the inset for the polymer (PαMS), the hexamer, and the 50% PαMS blend.

There are two concerns with the previous DSC studies [25,26]. The measurements are non-isothermal scans, involving a cooling scan followed by a heating scan at a certain scanning rate. A direct consequence is that if the dynamics of the blends have different temperature dependences from the pure components, according to the TNM (Tool-Narayanaswamy-Moynihan) model [40–42], the breadth of the glass transition (i.e., the temperature breadth) and the height of the associated enthalpy overshoot will change (details are shown later). The second concern is that the calorimetric relaxation arises only from local motions, limiting our understanding of the blending effects on the full relaxation response. Based on these two concerns, isothermal rheological measurements are expected to provide more information on the effects of blending. However, as noted earlier, throughout the literature reported in this area, dynamics in the T_g region of miscible blends have not received much attention. Only a few studies are available in this subject: Plazek and coworkers measured creep and recovery for long chain polystyrene blended with its short chains [24] and for solutions of polystyrene in tri-*m*-tolyl phosphate [14,16]; Adachi and Ishida measured dielectric relaxation of concentrated solutions of poly(vinyl chloride) in tetrahydrofuran [23] and Ngai analyzed these dielectric data to study the temperature dependence of the dynamics [43]; Roland and coworkers also studied dielectric relaxation of long chain polybutadiene mixed with its short chains [44]. These studies indicate that polymer solutions have weaker temperature-dependent α relaxations than their pure polymers [16,24,43] and the segmental relaxations of the blends are barely changed upon mixing [24,44], which further motivates the present study of the isothermal rheological response of our previously studied binary blends.

The objective of the present work is to investigate the viscoelastic properties of poly(α -methyl styrene)/oligomer blends through the glass transition region and compare these to those for the individual components. We determine the effect of oligomer concentration on the temperature dependence of the segmental dynamics, examine the validity of time–temperature superposition and the shape of the α relaxation for each blend composition, and characterize the effects of concentration on the rubbery plateau

and terminal relaxation regimes. The implication of the results with the temperature broadening of the calorimetric T_g is also discussed.

2. Experimental

2.1. Materials

A high molecular weight poly(α -methyl styrene) (PαMS) and its hexamer were obtained from Polymer Source, Inc. (Dorval, Canada). The number average molecular weight (M_n) and polydispersity index (PDI) of the materials are tabulated in Table 1, where the $PDI = M_w/M_n$ indicates the molecular weight distribution. Before use and to remove any adventitious moisture, the pure components were placed in a vacuum oven for 24 h at 70 °C for the polymer and at room temperature for the hexamer. The materials were stored under desiccant when not in use.

Three bimodal blends were prepared using the high molecular weight poly(α -methyl styrene) (PαMS) and the hexamer. The polymer concentrations in the blends are 25%, 50%, and 75% by weight, and the blends are designated as 25% PαMS, 50% PαMS, and 75% PαMS, respectively. A freeze-drying method was used to ensure that the blends were well mixed: first, three solutions of 10 wt% solute concentration were made in benzene (HPLC grade, Aldrich) and allowed to equilibrate at room temperature for 24 h. Then, each solution was solidified by swirling the solution in a glass vial placed in a dry ice/acetone bath; the frozen solutions were kept in the bath for another 15 min. A vacuum (0.05 torr) was then applied to the samples to sublime off the benzene. During the first 1 h when most of the solvent was removed, the sample temperature was maintained between –15 and –10 °C. Then the samples were exposed to vacuum (0.05 torr) for an additional 1 h at room temperature, before further vacuuming for another 20 h at 35 °C. Previously work [26] shows that an additional 24 h vacuuming at 50 or 70 °C did not change either the sample weight or the sample T_g , and hence the freeze-dried blends presumably have no residual solvent remaining. The calculated number- and weight-average molecular weights of the blends and the measured nominal T_g (at 10 °C/min) are shown in Table 1. The blends were also stored under desiccant when not in use.

For rheological measurements, disk-like samples of 8 mm diameter and 1.3 ± 0.3 mm thickness were used for parallel plate rheometry. The polymer and blend samples were molded using a Carver Hydraulic Press under a load of 10000–15000 pounds, depending on the sample. The polymer was molded 25 °C above its nominal T_g for 3 h. The blends were molded 40 °C above their T_g s for 2 h. Prior to the molding, the samples were vacuumed overnight at room temperature in a vacuum bag in order to minimize the presence of oxygen. After molding, samples were allowed to free cool to room temperature. For the hexamer, since it is too brittle to mold, the rheological sample was made directly inside the rheometer by loading the sample at room temperature under N_2 purge, then gradually heating the sample to 40 °C above its T_g and moving the upper plate up and down to form a disk-like sample. All

Table 1
Characteristics of the poly(α -methyl styrene), its oligomer, and their blends.^a

Sample	M_n (kg/mol)	PDI	T_g (°C)
Hexamer	0.769	1.16	37
PαMS	100.3	1.05	170
25% PαMS	1.022	26.4	57
50% PαMS	1.526	34.8	87
75% PαMS	3.007	26.3	127

^a For the blends, M_n and PDI are calculated values. The T_g values reported are T_g^i values obtained on heating after cooling at 10 °C/min.

of the polymer and blend samples were stored under desiccant when not in use; for the hexamer, a new sample was made for each experiment.

2.2. DSC measurements

Differential scanning calorimetry (DSC) measurements were performed on the polymer, the hexamer, and the blends using a Mettler-Toledo DSC823 with a Freon cooler. All runs were made under nitrogen atmosphere. Sample sizes ranged from 4 to 7 mg, and standard aluminum pans were used. The limiting fictive temperature, T_f^* , was determined using Star (Mettler-Toledo DSC823) software from DSC heating scans made at 10 °C/min after cooling at 10 °C/min from 40 °C above T_g . The limiting fictive temperature only depends on the cooling rate and is known to be approximately equal to the glass transition temperature, T_g , measured on cooling at the same cooling rate [45,46].

Temperature and heat flow calibrations were performed upon heating at 10 °C/min with indium ($T_m = 156.6$ °C, $\Delta H = 28.45$ J/g), gallium ($T_m = 29.78$ °C), and a liquid crystal standard (+)-4-n-hexyloxyphenyl-4'-(2'-methylbutyl)-biphenyl-4-carboxylate [47] (CE-3 from T.M. Leslie, University of Alabama; smectic to cholesteric transition at 78.8 °C). The temperature and heat flow are considered to be within ± 0.10 °C and ± 0.60 J/g. The calibrations were checked at regular intervals during the DSC studies by performing check runs using the above calibration materials.

2.3. Rheological measurements

Dynamic measurements were performed on the blends and their pure components under nitrogen atmosphere using two rheometers, a Paar-Physica MCR501 from Anton Paar and an Advanced Rheometric Expansion System (ARES) from TA Instruments. Our initial data was obtained using the MCR501 but we had difficulties obtaining the glassy moduli due to material slippage. We then used the ARES because the disposable aluminum platens on this instrument seemed to prevent slip. We then found differences in the data between the instruments after our initial compliance corrections so we repeated the experiments at all but the highest temperatures using the ARES. Instrument compliance corrections were then re-performed (see below) and the two data sets were found to be consistent.

Measurement frequencies ranging from 0.01 to 30 Hz were typically used. Slightly lower frequencies of the order of 0.001 Hz were also used for the polymer at 195 °C to obtain long time behavior and to avoid degradation that could occur at higher temperatures. The testing temperatures ranged from a few degrees below to 30–50 °C above the relevant T_g s. Samples were loaded at room temperature onto the 8 mm parallel plate platens before gradually being heated to $T_g + 40$ °C and held at that temperature for at least 20 min to get good contact between the material and the platens. Then, at each testing temperature higher than $T_g + 5$ °C, the sample was further held for at least 15 min to remove the thermal history and allow thermal equilibration. For the runs made at lower temperatures ($T \leq T_g + 5$ °C), Struik's protocol [48] was followed to minimize the influence of physical aging on the testing results: the sample was held at the testing temperature for 30–40 min before the application of strain, and then measurements were made in less than 3 min. To ensure a linear viscoelastic response, a small strain, $0.01\% < \gamma_0 < 1\%$, was applied to the sample.

Instrument compliance corrections were made for the dynamic data obtained from both the ARES and the Anton Paar MCR501 instruments. Following the method proposed by Schröter et al. [49], we calculated the actual modulus from the following two equations:

$$\frac{1}{K_{\text{meas}}^*} = \frac{1}{K_{\text{instr}}^*} + \frac{1}{K_{\text{sample}}^*} \quad (1)$$

$$K = \frac{G\pi}{2R^4h} \quad (2)$$

where K_{meas}^* is the measured complex torsional stiffness, K_{sample}^* is the actual complex sample torsional stiffness, and K_{instr}^* is the instrument torsional stiffness, which is assumed to be purely elastic. The torsional stiffness K is related to the shear modulus G , the radius of the platen R , and the gap between the platens h . For the ARES measurements, the correction was applied directly to the raw data of torque, twist, and phase angle obtained from the instrument software. An instrument compliance of 8.012×10^{-3} rad/Nm was used [50]. For the MCR501 measurements, we back-calculated the real strain and deflection angle to produce “raw” data assuming no instrument compliance and then applied the compliance correction [49] as described in equations (1) and (2). For the MCR501, an instrument compliance of 7.27×10^3 rad/Nm was used in the correction, slightly higher than the sum of the values used in the Anton Paar software of 3.25×10^3 rad/Nm for the tool compliance and 2.25 for the measuring cell (drag cup motor) compliance.

After compliance correction, the moduli obtained from MCR501 and ARES instruments show the same behavior, but to superpose master curves for the two sets of data a horizontal shift of, 0.04–0.68 decades is needed depending on the sample, presumably due to the temperature differences between the two instruments. Assuming an accurate temperature for the MCR501, the ARES data are accordingly shifted to determine the temperature for the ARES data. The temperature difference associated with the horizontal shift was 0.8–4.1 °C and depends on the temperature range used for each sample.

3. Results

The T_g of the PzMS, the hexamer, and their blends is plotted in Fig. 1 as a function of the polymer concentration along with the normalized heat capacities obtained on heating shown as the inset. Apparently, upon mixing, the glass transition broadens and the associated enthalpy overshoot decreases. In spite of these dramatic changes, the determined T_g s can still be well predicted by a recent model developed by Pinal et al. [51] for athermal mixtures. The model [51] is based on the mixing entropy concept and can be expressed as:

$$T_{gm} = T_{CK} \exp \left(- \frac{\Delta S_{\text{mix}}^c}{\Delta C_{pm}} \right) \quad (3)$$

$$\ln T_{CK} = \frac{w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \quad (4)$$

$$\Delta C_{pi} = C_{pi}^l - C_{pi}^g \quad i = 1, 2; \Delta C_{pm} = w_1 \Delta C_{p1} + w_2 \Delta C_{p2} \quad (5)$$

where T_{gm} , T_{g1} , and T_{g2} are the glass temperatures of the mixture (m), the oligomer (1), and the polymer (2), respectively; in the model, the term T_{CK} is equivalent to what is calculated from the Couchman–Karasz equation [52]; ΔC_{pm} , ΔC_{p1} , and ΔC_{p2} are their corresponding heat capacity changes at T_g , which can be related to the absolute heat capacity in the glass and liquid states, C_g^* and C_p^* available in the literature [25]; w_1 and w_2 are the weight percents of the oligomer and polymer in the blend; ΔS_{mix}^c is the configurational mixing entropy, which can be calculated from the Flory–Huggins equation [53,54]. Assuming no interaction between the oligomer and the polymer, the following equation is used:

$$\Delta S_{\text{mix}}^c = -k(N_1 \ln \phi_1 + N_2 \ln \phi_2) \quad (6)$$

where k is the Boltzmann constant, N_1 and N_2 are the number of the oligomer and polymer molecules, respectively, ϕ_1 and ϕ_2 are the volume fractions, assumed to equal to the weight fractions. Clearly, without any fitting parameters, this model gives an accurate prediction (i.e., within 1.4 ± 2.1 °C) for the T_g of our mixtures. Note that, in previous work [26], T_g fits from the Fox [55], Kelley-Bueche [56], and Kwei [57] equations were made for a similar system, poly(α -methyl styrene) blended with its pentane. We found that only the Kwei equation [57] accurately describes the experimental T_g s. On the other hand, the Kwei equation [57] contains two fitting parameters and the physical meanings of these parameters are not clear. Considering this, the Pinal equation [51] is more predictive.

The storage modulus and loss modulus as a function of frequency for the poly(α -methyl styrene) are shown in Figs. 2 and 3, along with the reduced master curves at 180 °C. For clarity, only nine of the runs made at temperatures between 160 and 195 °C are plotted. The T_g of this material is 170 °C as measured by DSC at a cooling rate of 10 °C/min. At the lowest temperatures and high frequencies, the material shows a glassy response; the glassy modulus is $\sim 10^9$ Pa, comparable with that found previously for poly(α -methyl styrene) [58]. As temperature increases and with decreasing frequency, the relaxation dispersion is observed. The material shows a rubbery plateau at 195 °C and approximately 0.03 Hz, followed by terminal relaxation. The loss modulus also goes through a maximum as the temperature decreases through the T_g region. The master curves were constructed by first applying a horizontal shift factor as determined from superimposing the loss tangent ($\tan \delta$) and then vertical shifts were made; since $\tan \delta$ is the ratio of G'' to G' , this procedure eliminates the influence of the vertical shift factor on the horizontal shifts.

Master curves of G' and G'' are plotted in Figs. 4 and 5 for all of the samples with reference temperatures indicated. The curves are positioned horizontally on the x-axis such that their segmental relaxations overlap. For the hexamer, the reference temperature is 10 °C above its nominal DSC T_g , but for the blends and the polymer

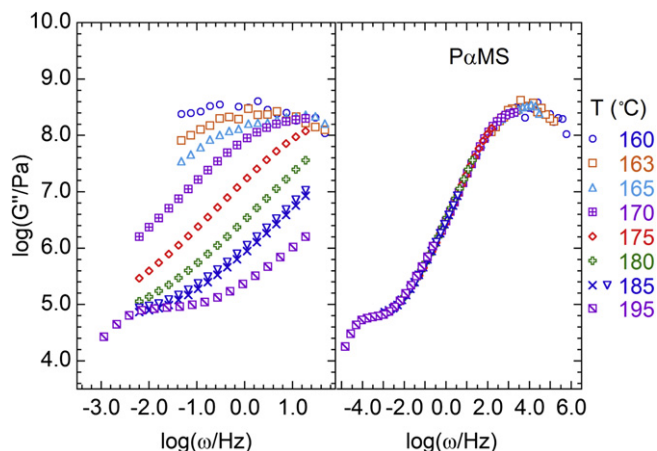


Fig. 3. Loss modulus as a function of frequency for the poly(α -methyl styrene) (P α MS) at temperatures ranging from 160 to 195 °C. The master curve at $T_{\text{ref}} = 180$ °C obtained from time–temperature superposition is shown on the right.

the reference temperatures are 12, 9, 4, and -1 °C higher than their DSC T_g s, respectively. The systemic variation indicates that the rheological T_g differs slightly from that measured by DSC, which might be expected since different techniques weigh the relaxation time distribution differently [46]. The well constructed master curves indicate that the time–temperature superposition (TTS) principle not only works for the pure materials but also for the blends. (We note that the shift is for the segmental relaxation since the terminal response was obtained only at one or two temperatures.) Consistent with our work, TTS has also been found to be valid for polymer solutions of polystyrene in tri-*m*-tolyl phosphate [15], block copolymers of poly(α -methyl styrene)-block-polystyrene [5], and polymer/polymer blends, including both weakly interacting blends such as polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide) [7], high molecular weight 1,4-polybutadiene/low molecular weight 1,4-polybutadiene [1,6,8], and long chain polystyrene/short chain

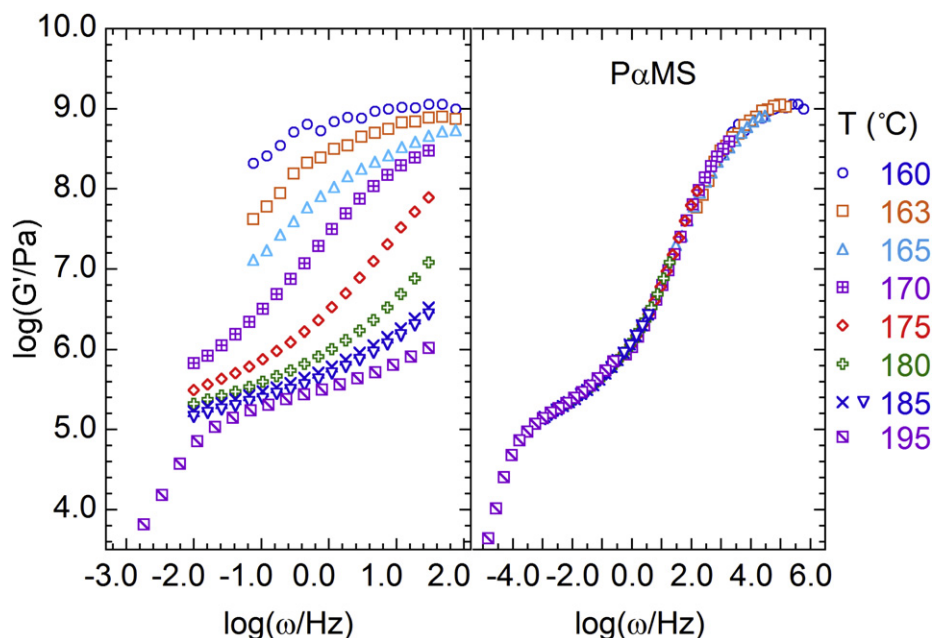


Fig. 2. Storage modulus as a function of frequency for the poly(α -methyl styrene) (P α MS) at temperatures ranging from 160 to 195 °C. The master curve at $T_{\text{ref}} = 180$ °C obtained from time–temperature superposition is shown on the right.

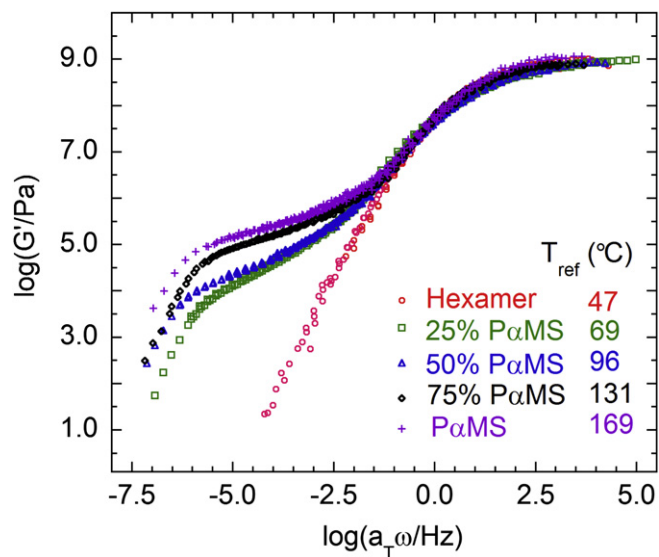


Fig. 4. Master curves of storage modulus G' plotted as a function of frequency for the hexamer, the blends (25/75, 50/50, and 75/25), and the poly(α -methyl styrene) (P α MS). The reference temperatures are indicated in the figure.

polystyrene [14,24], and more strongly interacting systems such as the hydrogen-bonding poly(4-vinyl phenol)/poly(ethylene oxide) blend [7]. However, failure of the principle is also reported for 1,2-polybutadiene/polyisoprene mixtures [2], and for low molecular weight polystyrene in tri-*m*-tolyl phosphate solutions [16].

Figs. 4 and 5 also show that the glassy modulus and, more importantly, the breadth of the α relaxation are unchanged with blending. Both of these observations are in good agreement with Plazek and coworkers' findings [24]: binary blends of a high and a low molecular weight polystyrene showed the same glassy compliance and similar glassy dispersion as those of the pure components. The unchanged breadth of the α -dispersion is also consistent with a recent study of polybutadienes by Bogoslovov et al. [44] in which mixtures of long and short chains, giving the same number average molecular weight, exhibited the same shape

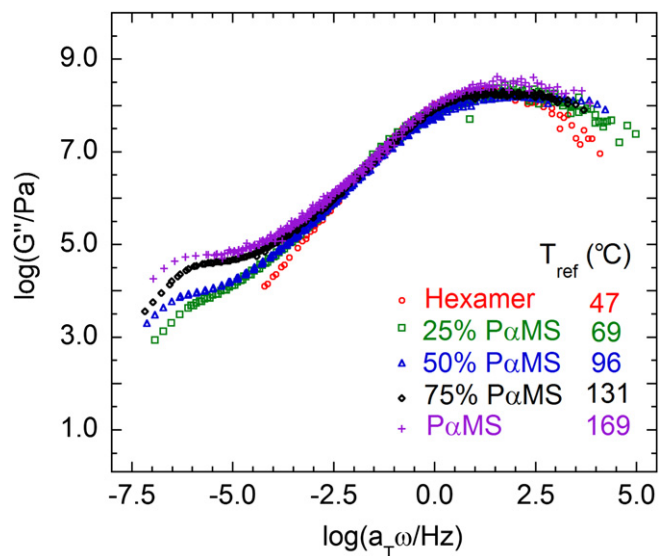


Fig. 5. Master curves of loss modulus G'' plotted as a function of frequency for the hexamer, the blends (25/75, 50/50, and 75/25), and the poly(α -methyl styrene) (P α MS). The reference temperatures are indicated in the figure.

segmental or α relaxation. However, the results for the breadth of the α relaxation differ from the interpretation of our previous DSC measurements where obvious temperature broadening in T_g is observed [25,26], as shown in the inset of Fig. 1. The reasons for the differences are discussed later.

The plateau modulus G_N^0 for the pure components and blends was determined and the results are shown in Fig. 6. We calculated the plateau from the storage modulus at the frequency where $\tan\delta$ is a minimum. Among many other applicable methods, this is one that is frequently used when the minimum of $\tan\delta$ is available [5,7,59]. The polymer exhibits a plateau of 1.6×10^5 Pa, slightly lower than the literature [22] value of 2.4×10^5 Pa for 6.85×10^6 and 2.71×10^6 g/mol molecular weight poly(α -methyl styrene)s, which was obtained from extrapolating the plateau modulus of the poly(α -methyl styrene) solutions in a mixture of chlorinated biphenyl to a polymer concentration of 1. The length of the plateau increases with increasing polymer concentration, which agrees with other studies [15,60,61]. To better understand the dynamics of polymer chains in entangled solutions and to test the scaling reported in the literature, the concentration dependence of the plateau modulus is determined. The plateau modulus is found to scale with the weight concentration of polymer (ϕ) as $G_N^0 \propto \phi^{2.04 \pm 0.32}$. The scaling parameter is consistent with reported values of 2.0–2.33 [12,19,62–65]. In particular, the results agree with recent findings from Heo et al. [12] and Colby et al. [19] that for θ solvent conditions, which is the case for our system [66], the scaling parameter is expected to be around 2.30–2.33 over the entire concentration range [12,19]. It is noted that the same scaling applies to good solvents but for different reasons [12,19]. In addition to the scaling of the rubbery plateau, the concentration dependence of the terminal relaxation time (τ_d) is also examined. From the G' curves shown in Fig. 4, we found that τ_d scales with polymer concentration as $\tau_d \propto \phi^{1.35 \pm 0.33}$. The exponent is expected to be from 1.4 to 1.7 from the Ngai coupling model, consistent with our data and the other scant data in the literature, whereas reptation gives a much weaker scaling [67].

The horizontal shift factors used to construct these master curves are shown in Fig. 7 for the polymer, the hexamer, and the 75/25 blend. For the sake of clarity, the data for the other two blends are not shown. The Vogel-Fulcher-Tammann [68–70] (VFT) equation was used to describe the data; the best fits are shown as solid lines. The equation can be written as:

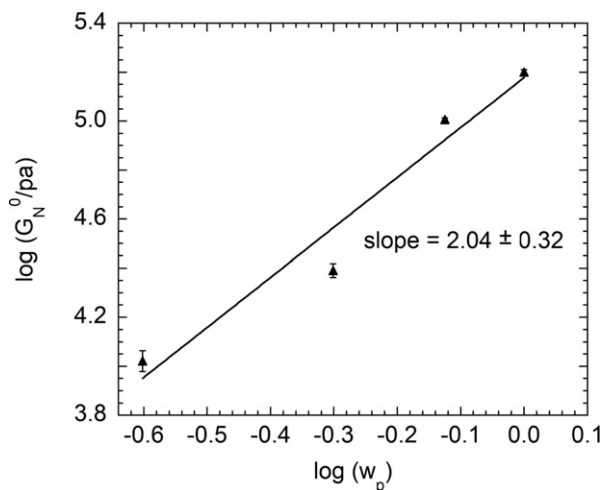


Fig. 6. Logarithmic plot of the rubbery plateau modulus as a function of the polymer weight percent w_p . Solid line is the best linear fit.

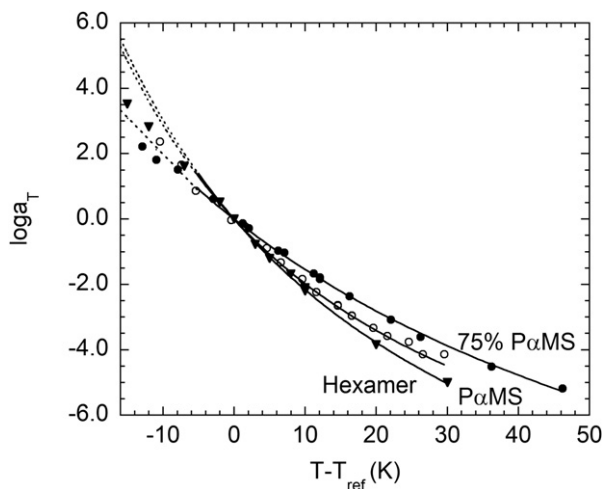


Fig. 7. Shift factors used to construct the master curves for the hexamer, the 75/25 blend, and the poly(α -methyl styrene) (P α MS) plotted as a function of the temperature departure from the reference temperature. Lines are the best fits from Vogel–Fulcher–Tammann equation [68–70].

$$\ln a_T = \frac{B}{T - T_\infty} - \frac{B}{T_{\text{ref}} - T_\infty} \quad (7)$$

where a_T is the shift factor required at temperature T relative to the reference temperature T_{ref} , T_∞ is the VFT temperature, and B is a constant. Compared to the pure components, the shift factors obtained for the blends, especially for the 75/25 one, show a weaker temperature dependence. The temperature dependence of the relaxation times at $T_{\text{ref}} - 10^\circ\text{C}$ is shown in Fig. 8, along with those obtained from DSC measurements at the DSC T_g for poly(α -methyl styrene)/oligomer [26] and polystyrene/oligomer blends [71]. The rheological data agree with the DSC results, and for both poly(α -methyl styrene) and polystyrene systems, the temperature dependence is $30 \pm 5\%$ lower for the blends, compared to the pure polymer. We note that, compared to the pure polymer, a weaker temperature dependence of the α relaxation was also found for long chain polystyrene blended with its

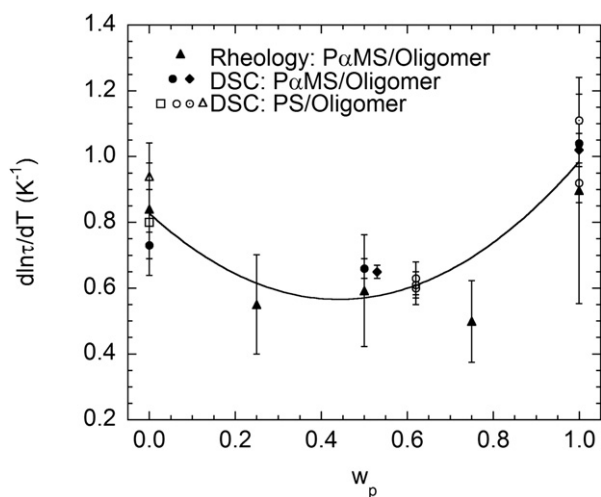


Fig. 8. Temperature dependence of relaxation time at $T_{\text{ref}} - 10^\circ\text{C}$ for the rheological data of poly(α -methyl styrene)/oligomer system, along with those obtained from DSC measurements at their T_g for poly(α -methyl styrene)/oligomer [26] and polystyrene/oligomer blends [71].

short chains [24], solutions of polystyrene in tri-*m*-tolyl phosphate [16], and solutions of poly(vinyl chloride) in tetrahydrofuran [43]. Whether this weaker temperature dependence is the reason for the broadening of T_g as observed by DSC, is discussed subsequently.

4. Discussion

The results presented above demonstrate a seeming discrepancy between rheological studies of blend dynamics and those of DSC measurements: the shape of the segmental relaxation as measured by the rheological response seems to be little changed upon mixing but the calorimetric transition seems to dramatically broaden and the associated enthalpy overshoot appears to be strongly depressed. The question that arises is “why?”

One possibility is that the temperature dependence of the segmental dynamics is weaker in the blends, as shown in Figs. 7 and 8. Given that the calorimetric transition is generally measured on heating or cooling, a change in the temperature dependence of the relaxation times is known to affect the temperature breadth of the transition and the magnitude of the enthalpy overshoots. For example, blends with weaker temperature dependence require a broader temperature range to vitrify. In order to determine whether the change in $d \ln \tau / dT$ ($\sim 30\%$) is sufficient to explain the changing T_g breadth in DSC measurements, we used the TNM (Tool–Narayanaswamy–Moynihan) model of structural recovery [40–42] to examine the influence of changes in the temperature dependence on the breadth of the transition and the height of the enthalpy overshoot.

The TNM model can quantitatively describe all behaviors related to structural recovery and the glass transition [72,73]. The approach successfully captures both the nonexponential and nonlinear nature of structural relaxation. To model DSC scans, one calculates the normalized heat capacity (C_{pN}), which is simply the temperature derivative of the fictive temperature, T_f . The relaxation function used in the TNM constitutive model is of the form of a Kolrausch–Williams–Watt (KWW) function [74,75] and the response of the heat capacity is determined from:

$$C_{pN} = \frac{dT_f}{dT} = 1 - \exp \left[- \left(\int_0^t \frac{dt}{\tau_0(T, T_f)} \right)^\beta \right] \quad (8)$$

where T is the temperature which is a function of time in a given DSC scan history, β is the degree of nonexponentiality, and τ_0 is the relaxation time which is a function of T and T_f . In the TNM model, the temperature and structure dependence of relaxation time are given by:

$$\ln \tau_0 = \ln A + \frac{x \Delta h}{RT} + \frac{(1-x) \Delta h}{RT_f} \quad (9)$$

where A is a constant, Δh is the apparent activation energy of the relaxation process ($\cong (d \ln \tau) / (d(1/T))|_{T_g}$), x is the non-linearity parameter which partitions the temperature and structure dependence of the relaxation time, and R is the gas constant. Here we used software developed by Sobieski [76] which implements the TNM model and allows us to simulate DSC heating curves for different values of the TNM parameters $\Delta h/R$ and x .

The thermal history we used consisted of cooling at $10^\circ\text{C}/\text{min}$ from 60°C higher than T_g to 60°C lower than T_g and heating from $T_g - 60^\circ\text{C}$ to $T_g + 60^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$. In the simulation, we varied the parameter of $\Delta h/RT_g^2$ ($\cong d \ln \tau / dT$ at T_g) from 0.65 to 0.45, 0.30, and 0.20 K^{-1} , which corresponds to a change of 31%, 54%, and 69%,

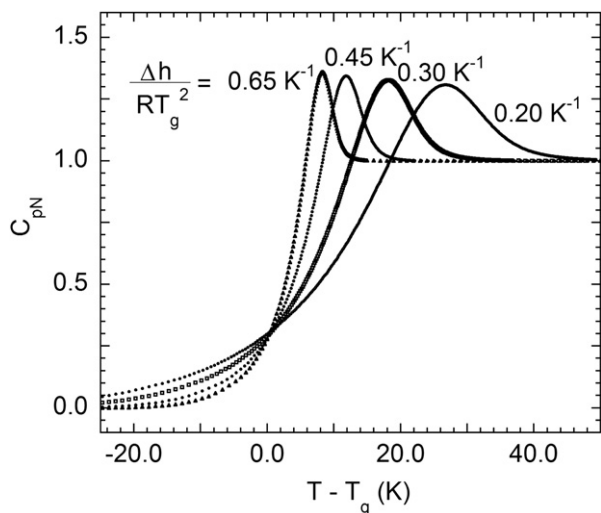


Fig. 9. TNM model [40–42] prediction on the normalized heat capacity C_{pN} on heating from $T_g - 60$ °C to $T_g + 60$ °C at 10 °C/min after cooling at 10 °C/min.

respectively, in $\ln\tau/dT$; all of the other parameters were kept constant. The simulated normalized heat capacities obtained on heating are shown in Fig. 9 as a function of the temperature departure from T_g . Clearly, the weaker temperature dependence does broaden the transition and does reduce the enthalpy overshoot. However, the influence of the temperature dependence of the relaxation times is too weak to account for the observed experimental data (see Fig. 1) in which dramatic reductions in the enthalpy overshoots are observed for the blends. Based on the TNM calculations, the 30% change in $\ln\tau/dT$ observed experimentally for the blend (see Fig. 8) cannot explain the temperature broadening observed in the DSC scans nor the dramatic changes in the enthalpy overshoot.

If the concentration dependence of the activation energy cannot explain the changing temperature breadth of the T_g of the blends, what can? Within the context of the TNM model, there are three possibilities related to the parameters, Δh , β , and x . We have just shown that the concentration dependence of the activation energy for the segmental relaxations (related to Δh) is

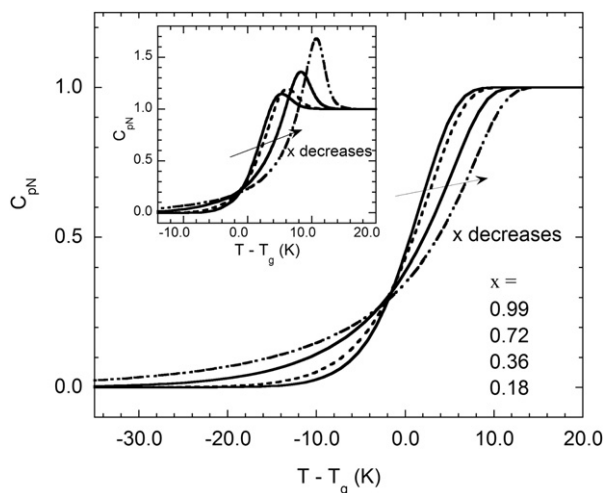


Fig. 10. TNM model [40–42] prediction on the normalized heat capacity C_{pN} on cooling from $T_g - 60$ °C to $T_g + 60$ °C at 10 °C/min after cooling at 10 °C/min. Prediction on the C_{pN} on heating is also shown as the inset.

insufficient to explain the broadening. The rheological results also show that the shape of the relaxation time distribution (related to β) itself does not change since, i.e., time–concentration superposition of the segmental relaxations is observed. Thus, within the context of the TNM model, only one parameter remains that could explain the results, that is the non-linearity parameter x .

As already mentioned, x partitions the temperature T and structure T_f dependence of the relaxation time. Then, for a given activation energy, a smaller value of x leads to a stronger dependence of the relaxation time on the glassy structure T_f . Fig. 10 shows the results of simulation for C_{pN} in both cooling and heating (inset) histories and for which only the non-linearity parameter x was varied. Decreasing x broadens the DSC cooling curves. However, a decrease in x also leads to larger overshoots on heating (inset), which differs from the experimental observations for blending (Fig. 1). Whether this discrepancy can be attributed to previously identified problems with the TNM model [73,77–79] is not clear.

5. Conclusion

The viscoelastic properties of poly(α -methyl styrene), its hexamer, and their athermal blends at various concentrations are studied. Master curves for the dynamic shear responses, G' and G'' , are successfully constructed for both the pure materials and the blends, indicating the validity of the time–temperature superposition principle. The rubbery plateau modulus scales with the polymer concentration as $G_N^0 \propto \phi^{2.04 \pm 0.32}$, and the length of the plateau increases with increasing polymer concentration. The terminal relaxation time scales with the polymer concentration as $\tau_d \propto \phi^{1.35 \pm 0.33}$. Both of these scalings are consistent with literature reports. The temperature dependence of the shift factors follows the Vogel–Fulcher behavior over the temperature range studied, and the dependence is slightly weaker for the blends. The shape of the segmental relaxation spectrum appears unchanged by concentration, contrasting with calorimetric studies where the polymer/oligomer blends show obviously temperature-broadened glass transitions and depressed enthalpy overshoots. The effects of the weaker temperature dependence on the segmental dynamics were further examined by using the TNM (Tool–Naraswamy–Moy-nihan) model of structure recovery. The results show that the change in the temperature dependence is not sufficient to account for the temperature broadening observed in calorimetric studies. We conclude that the temperature broadening of the glass transition for our blends is not due to a broadening of the dynamic spectrum or to a change in the apparent activation energy.

The possibility that the temperature broadening of the blend dynamics arises from changes in the non-linearity parameter x of the TNM model was considered. While the broadening could be due to a decreasing value of x , we found that this same decrease would lead to increasing enthalpy overshoots, contrary to the experimental observations. The combination of the calorimetric results with the rheological measurements further indicates that the fundamental basis of the TNM-type of model of structural kinetics in glasses is potentially wrong and new models are needed to make further progress in this domain.

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