

Assessing the Range of Validity of Current Tube Models Through Analysis of a Comprehensive Set of Star-Linear 1,4-Polybutadiene Polymer Blends

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To supplement the analysis of star-linear blends featuring 1,4-polybutadiene stars of arm molecular weights near 24 kDa, shown in Figures 10-14 in the main text, we here present and analyze additional star-linear blend data sets. Specifically, we assess the ability of the Hierarchical model predictions, implemented with Das parameters and “thin tube” relaxation, consistent with the main text, to match rheological data for our new 1,4-polybutadiene star-linear blend series 44KS-13.3KL, 47KS-73KL, and 47KS-260KL, as well as previously published data for 42.3KS-105KL blends from Struglinski et al.^[1] We will refer to this group of blends containing star polymers with arm molecular weights of 42.3kDa, 44kDa, and 47kDa, as the “~40KS-linear blend sets.” Similarly, we will refer to the star-linear blends presented in Figures 10-14 of the main text, with star arm molecular weights of approximately 24kDa, 25.3kDa, and 25.4kDa, as “~20KS-linear blend sets.” For the ~40KS-linear blend sets, we conclude, in agreement with the findings presented in the main paper, that the accuracy of the Hierarchical model is poor for star-linear blends in which the pure linear component has terminal relaxation time less than, but within 3-4 orders of magnitude of that of the star component. In addition to exploring the ~40KS-linear blends sets, we also here provide a deeper analysis of the 24KS-

210KL and 25.3KS-260KL blends, respectively featured in Figures 12 and 13 in the main text, to determine whether or not polydispersity in the linear component significantly influences the non-monotonic dependence of terminal relaxation time on star volume fraction.

The SI is organized as follows. In Section I, we disclose details concerning the synthesis and characterization of the new 1,4-polybutadiene star and linear polymers in this study. In Section II.1, we report the WLF C_1 and C_2 coefficients of the pure stars and the pure linear polymers, as well as of the star-linear blends featured here in the SI and in the main text. In Section II.2, we analyze the accuracy of Hierarchical model predictions, using molecular weights defined by zero-shear viscosity fitting and GPC measurements, against the ~40KS-linear blend sets. In Section II.3 we report the G'' rheology of the ~20KS-linear blend sets that correspond with the G' data shown in Figures 10-13 in the main text. In Section II.4, we assess the dependence of the non-monotonicity referred to above on the presence of polydispersity in pure linear components of the 24KS-210KL and 25.3KS-260KL blends presented in the main text. In Section II.5, we compare predictions of the Branch-on-Branch (BoB) model originating from Das et al.^[2] with those of the Hierarchical model. In Section II.6, we investigate further the accuracy of non-monotonic model predictions by assessing select star-linear blends. In Section II.7, we assess Hierarchical model predictions, using the Constraint Release-Rouse (CR-Rouse) “fat tube” option, for select star-linear blends. Lastly, in Section II.8, we consider the effect of including density variations in vertical shifting to create master curves, and show that the effect is negligible.

I. SYNTHESIS AND CHARACTERIZATION OF STAR AND LINEAR 1,4-POLYBUTADIENE POLYMERS

I.1 73KL, 260KL, 25.3KS, 44KS and 47KS synthesis and characterization (Hadjichristidis Lab)

Chemicals. All chemicals were purified according to the standards required for anionic polymerization, using well-established high-vacuum procedures.^[3] 1,3-Butadiene (Sigma-Aldrich, 99%) was purified *via* consecutive distillations over *n*-BuLi, at -10°C using ice/salt bath, prior to addition to the polymerization reactor. Benzene (Sigma-Aldrich, 99.8%) was purified *via* distillation from CaH₂ and stored in a round bottom flask, under high vacuum. *sec*-Butyllithium (*s*-BuLi, 1.4 M in cyclohexane, Sigma-Aldrich) was used without purification and diluted with dry *n*-hexane. 1,2-bis(dichloromethylsilyl)ethane (Gelest, 95%) was purified by crystallization from *n*-hexane, followed by three crystallizations from the bulk and subsequently diluted in *n*-hexane and stored under high vacuum at -30 °C. Methanol (Sigma-Aldrich, 99.8%) (terminating agent) was stored under high vacuum and used as received.

Synthesis of linear 1,4-polybutadiene (PBd_{1,4}). A typical procedure for the synthesis of the linear PBd_{1,4} 73KL and 260KL melts is as follows.^[3,4,5] 7g of 1,3-butadiene was polymerized at room temperature, using 0.03 mmol of *sec*-butyllithium as initiator and benzene as solvent. The mixture was left to react for 1 day and finally, the polymerization quenched with methanol and the polymer precipitated in a large amount of methanol. The final product was dried in a vacuum oven until constant weight.

Synthesis of 1,4-polybutadiene (PBd_{1,4}) 4-arm stars. A typical procedure for the synthesis of the 4-arm star PBd_{1,4} 25.3KS, 44KS and 47KS melts is as follows.^[3,4,5] 10g of 1,3-butadiene was polymerized at room temperature, using 0.22 mmol of *sec*-butyllithium as initiator and benzene as solvent. The mixture was left to react for 1 day and then an aliquot was

taken by heat-sealing the corresponding constriction tube for molecular characterization. The rest of the “living” polymer solution was reacted with 0.044 mmol of 1,2-bis(dichloromethylsilyl)ethane (BMDCE). The linking reaction was monitored by GPC and lasted, depending on the sample, 2-3 weeks. After the completion of the reaction, the excess of the living chains were terminated by the addition of degassed methanol and the solution precipitated in a large amount of methanol. The 4-arm star PBd_{1,4} melts were purified from the unreacted linear chains by repeated solvent/non-solvent (toluene/methanol) fractionations.

Characterization. The weight average molecular weights (M_w) of all samples were determined using the light scattering detector on a triple detection GPC. THF was the eluent, at a flow rate of 1 mL/min at 30 °C. Refractive index increments, dn/dc , were measured with a Brookhaven BI-DNDCW refractometer, at 30 °C, calibrated with KCl solutions. Figures S1-A, S1-B, S1-C and S1-D feature the GPC curves of the 73KL, 260KL, 25.3KS and 47KS. ¹H-NMR spectroscopy measurements were carried out using CDCl₃ (Sigma-Aldrich, 99.6%) on a Brücker AV-500 spectrometer. Figures S2-A, S2-B, S2-C, and S2-D respectively feature the ¹H-NMR results of the pure 73KL, 260KL, 25.3KS and 47KS.

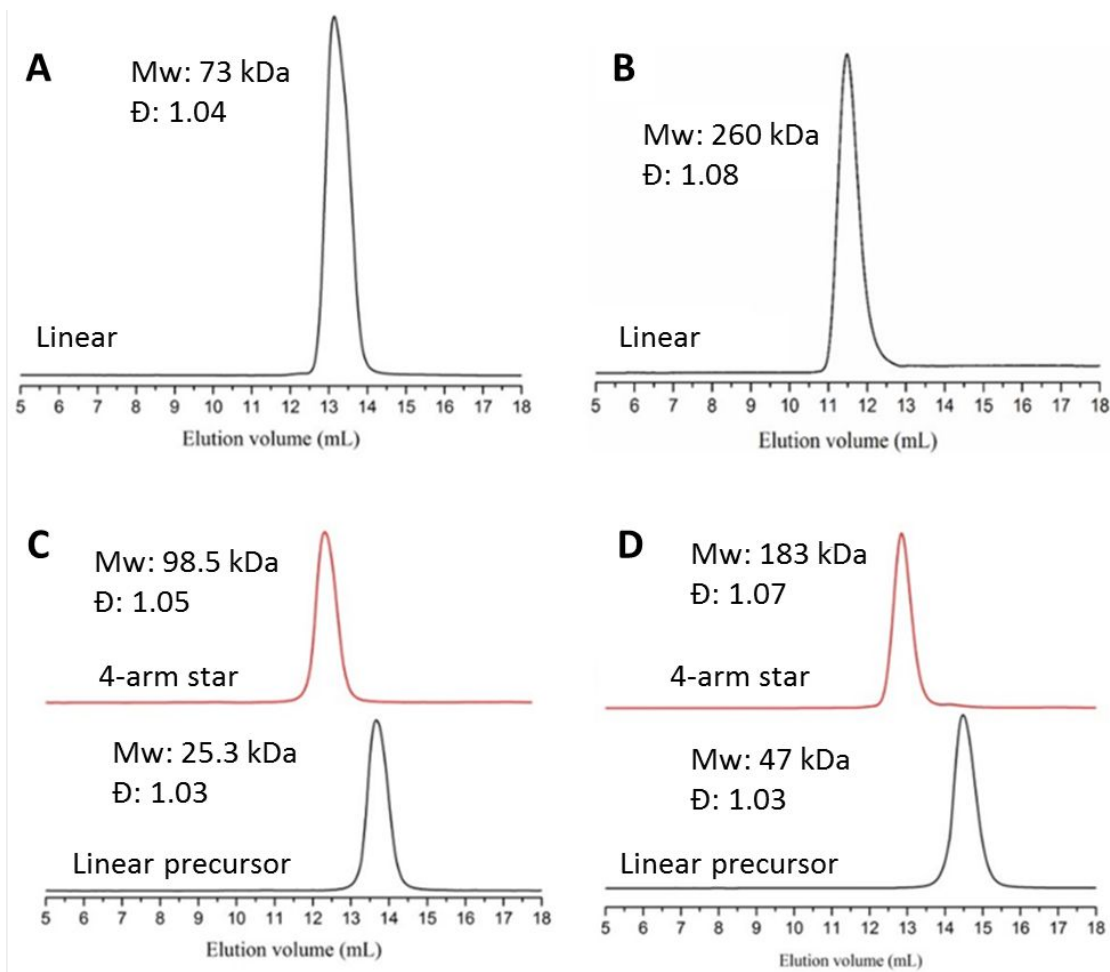


Figure S1: Gel permeation chromatography (GPC) of two linear and two four-arm star 1,4-polybutadienes A) 73KL, B) 260KL, C) 25.3KS, and D) 47KS. Also Included in C) and D) are the GPC curves of the linear precursors prior to branching synthesis of the 25.3KS and 47KS, respectively. The linear molecular weights (Mw) listed in Table 1 of the main text were determined by GPC, using a light scattering detector. The arm molecular weights of the stars, shown in parentheses in Table 1, were obtained by dividing the peak molecular weights by 4, which is the nominal number of arms per star molecule. Also reported here are the polydispersity (Đ) for each sample.

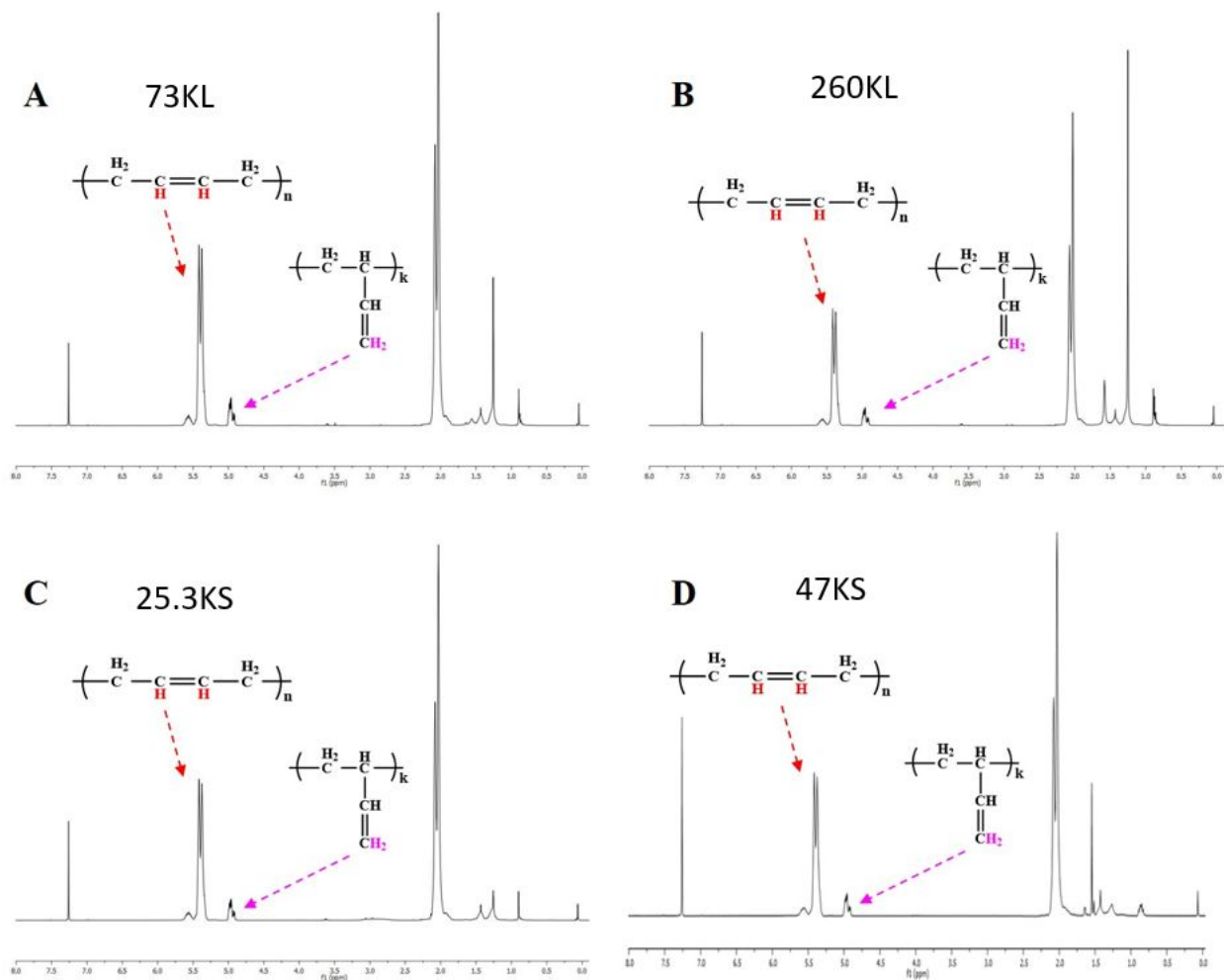


Figure S2: ^1H -NMR of 1,4-polybutadienes A) 73KL, B) 260KL, C) 25.3KS, and D) 47KS

I.2 GPC and TGIC measurements of the 4-arm star 44KS (Chang Lab)

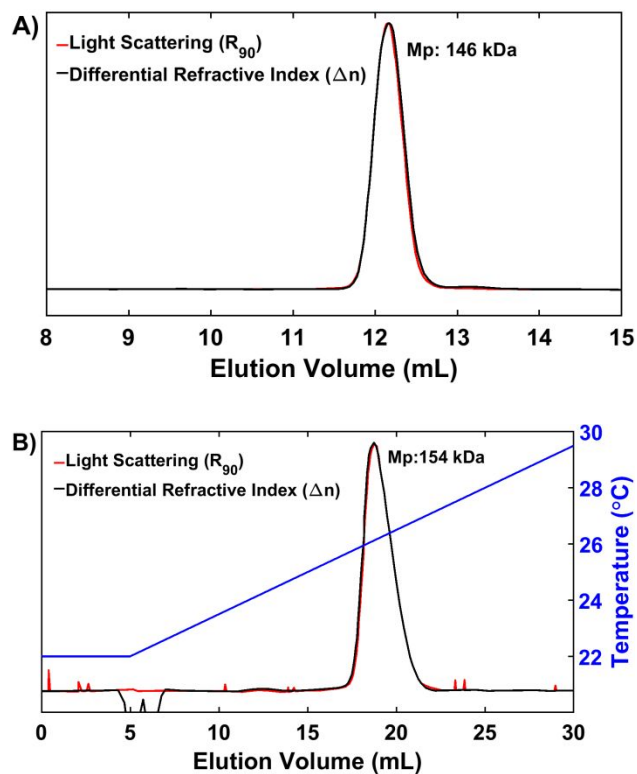


Figure S3: A) GPC and B) TGIC characterization of the 1,4-polybutadiene 4-arm star 44KS. The GPC and TGIC arm molecular weights observed in Table 1 of the main text were obtained by dividing the peak molecular weight, “Mp”, value depicted in the above figures by 4, which is the nominal number of arms per star molecule. The polydispersity index of this melt is 1.07, as reported in Table 1 of the main text.

I.3 GPC and H-NMR measurements of the linear 13.3KL (Mays Lab)

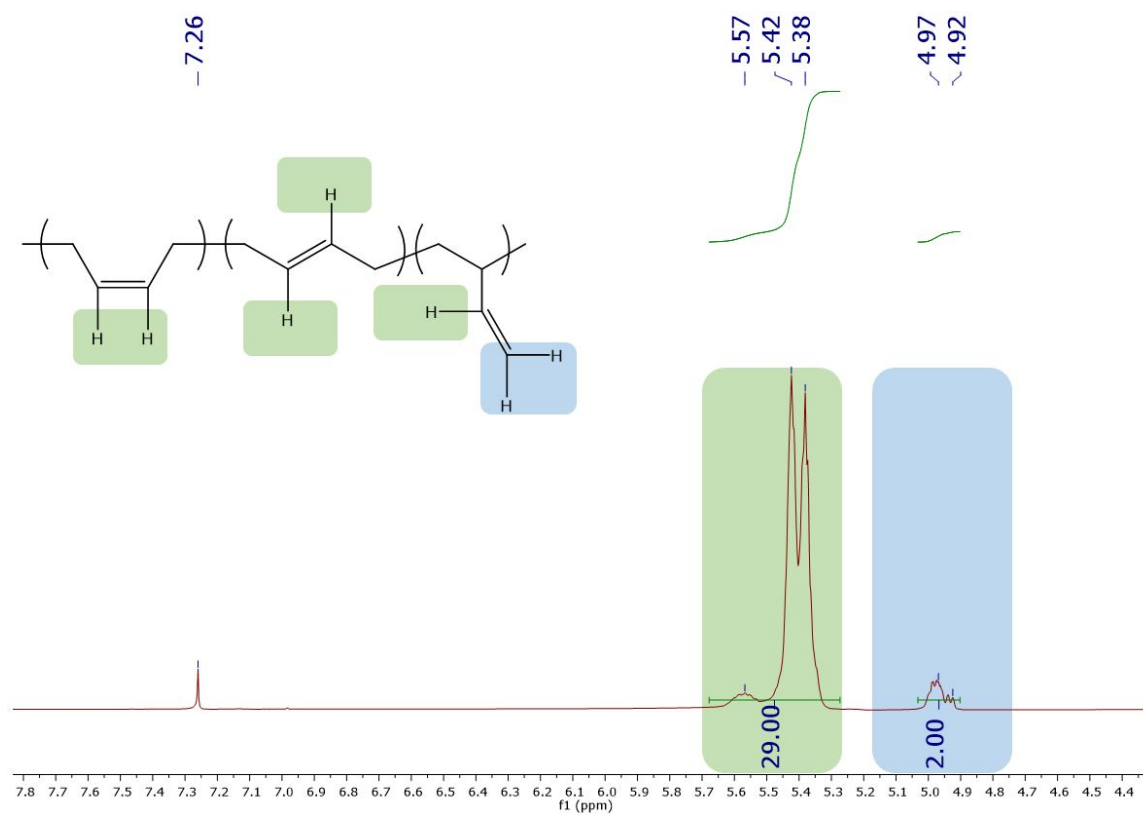


Figure S4: ^1H -NMR of the 1,4-polybutadiene 13.3KL

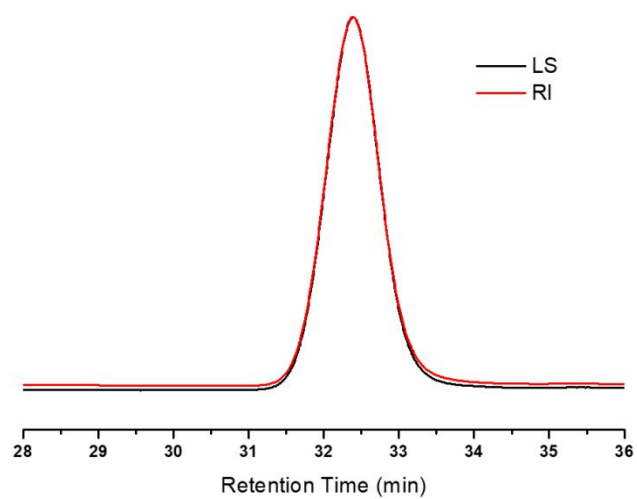


Figure S5: GPC measurements of the 13.3KL. The black line represents measurements conducted by light scattering; the red line is the refractive index (RI). The polydispersity index of this sample is 1.02, as reported in Table 1 of the main text.

II. RHEOLOGY OF 1,4-POLYBUTADIENE STAR-LINEAR BLENDS

II.1 Time-temperature superposition

In supplement to the plots of horizontal temperature shift factors depicted in Figures 1 and 2 of the main text, we report here the WLF C_1 and C_2 coefficients obtained from the shift factor curves of the pure star and pure linear 1,4-polybutadienes used in this study. We note that the C_1 and C_2 coefficients of the pure 105KL and 42.3KS samples taken from Struglinski et al.^[1] were not reported in the original work, and so are absent from Table S1. In Tables S2 and S3, we report the WLF C_1 and C_2 coefficients of the new 24KS-13.3KL and 44KS-13.3KL star-linear blends, respectively. For both of these star-linear blend series, the WLF C_1 and C_2 coefficients are organized by star volume fraction (ϕ_s).

Table S1: WLF time-temperature superposition constants C_1 and C_2 of the pure star and pure linear 1,4-polybutadienes. The reference temperature for all figures and tables featured in the main text and in this Supplemental Information, is 25°C.

Sample	Source	Architecture	C_1	C_2
7.5KL	Shivokhin et al. ^[6]	Linear	4.7	154.3
24.5KS		3-arm Star	4.7	154.3

58KL	Desai et al. ^[7]	Linear	3.9	178.9
24KS		4-arm Star	4.7	187.1
105KL	Struglinski et al. ^[1]	Linear	-----	-----
42.3KS		3-arm Star	-----	-----
13.3KL	Polymer Source	Linear	3.9	175.6
210KL		Linear	4.0	176.3
73KL	Fresh synthesis	Linear	3.9	169.9
260KL		Linear	4.2	174.3
25.3KS		4-arm Star	4.4	180.3
44KS		4-arm Star	5.0	194.4
47KS		4-arm Star	5.2	194.1

Table S2: The WLF C_1 and C_2 constants of the 24KS-13.3KL blend series.

Star volume fraction (ϕ_s)	C_1	C_2
1	4.7	187.1
0.8	4.8	188.3
0.4	4.4	183.1
0.1	4.2	181.5
0	3.9	175.6

Table S3: The same as Table S2, but for 44KS-13.3KL blend series.

Star volume fraction (ϕ_s)	C_1	C_2
1	5.0	194.4
0.9	5.0	194.2
0.8	4.8	197.0
0.6	4.8	195.0
0.4	4.6	189.2
0.2	4.3	185.3
0	3.9	175.6

II.2 Hierarchical model predictions of the 40KS-linear blend data

II.2.i Predictions using molecular weights defined by zero-shear viscosity fitting

Similar to Figures 10-14 in the main text that report the ~20KS-linear blend sets, we analyze in Figures S6-S9 how well the Hierarchical model, with Das parameters and thin tube CR-Rouse dynamics, predicts the rheology of the ~40KS-linear blend sets, including blends newly prepared here and data borrowed from the literature. However, in contrast to Figures 10-14 of the main text, the molecular weights of the pure star and the pure linear polymers used in model predictions in Figures S6-S14 are strictly based on zero-shear viscosity measurements, as shown in Table 5 of the main text. Model predictions of the ~40KS-linear blends sets with use of molecular weights defined by GPC are shown in the next Section.

Figure S6 shows that Hierarchical model predictions (lines) are in relatively good agreement with measurements (symbols) for the 44KS-13.3KL blends. However, in Figure S6-A,

the model predicts faster terminal relaxation of the $\phi_s=0.6$ blend by a factor of roughly 1.6, which increases to a factor of 2.4 for $\phi_s=0.2$. Similar modeling success is observed in Figure S7-A for the 47KS-73KL blends, for which faster relaxation by factors of roughly 1.5, 2.3, and 2.3 are predicted for $\phi_s=0.8$, 0.6, and 0.4, respectively. The success of model predictions in Figures S6 and S7 are consistent with the observations in the main text and in Desai et al.,^[7] which find that Hierarchical model predictions tend to agree with star-linear blend data when the terminal relaxation times of the pure star are at least 3-4 orders of magnitude longer than that of the pure linear. The terminal relaxation times of the pure star and pure linear 1,4-polybutadienes in Figure S6-A are in fact separated by roughly 5 orders of magnitude, while this separation is over 3 orders of magnitude in Figure S7-A.

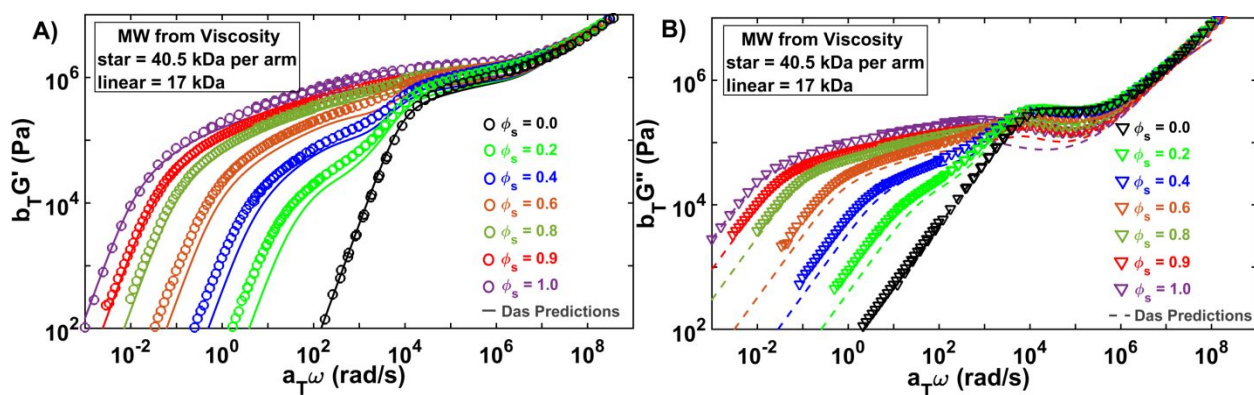


Figure S6: Experimental (symbols) A) G' and B) G'' linear rheology of the 44KS-13.3KL blend series at various star volume fractions ϕ_s , compared with predictions of the Hierarchical model (lines). The star and linear molecular weights used in the model predictions, listed in the legend, are from Table 5 of the main text.

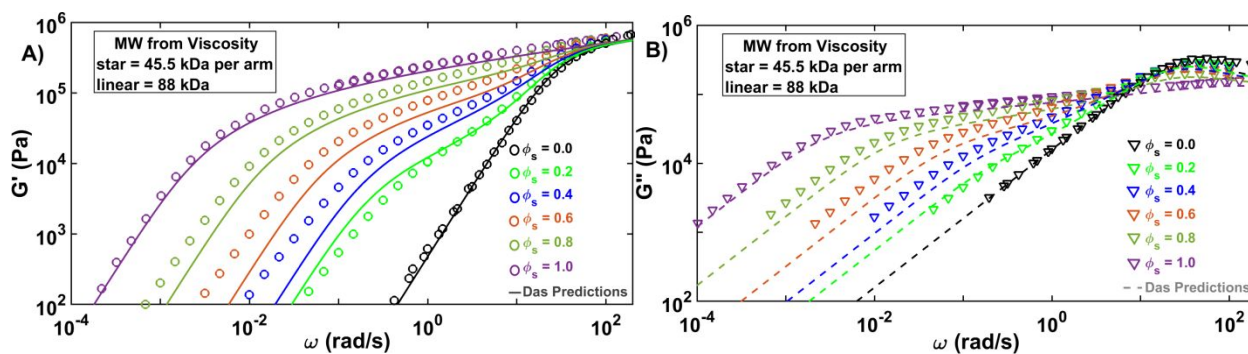


Figure S7: The same as Figure S6, but for the 47KS-73KL blend series.

Figure S8 shows, in contrast, a notable failure of the Hierarchical predictions (lines) for the 42.3KS-105KL rheological data (symbols) of Struglinski et al.^[1] The experimental data clearly show a monotonic dependence of terminal time on ϕ_s ; however, model predictions of the relaxation time of the $\phi_s=0.1$ blend is clearly longer than for the $\phi_s=0.75, 0.5, 0.3$ and 0.2 blend compositions. In addition, the relaxation time for the $\phi_s=0.2$ blend is longer than that for the $\phi_s=0.3$ blend. Besides the erroneously predicted non-monotonicity, the Hierarchical model also underpredicts the relaxation time for the $\phi_s=0.75$ blend by a factor of roughly 2.5. Unlike the 44KS-13.3KL and 47KS-73KL blends depicted in Figures S6-A and S7-A, the terminal relaxation of the pure 42.3KS star and the pure 105KL linear in Figure S8-A are separated by less than 3 orders of magnitude, which seems to correlate with the failure of the model.

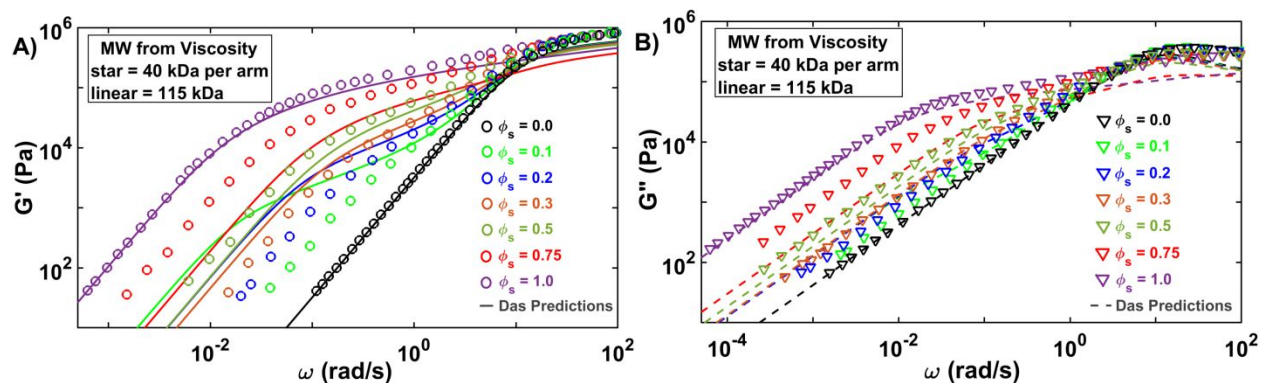


Figure S8: The same as Figure S6, but for the 42.3KS-105KL blend series, from Struglinski et al.^[1]

Figure S9 shows that the model predictions for the 47KS-260KL blends incorrectly predict a slight non-monotonicity. Given that the 24KS-210KL and 25.3KS-260KL blends, presented respectively in Figures 13 and 14 of the main text, show non-monotonic experimental behavior, we suggest that had the pure 47KS star been blended with a somewhat higher molecular weight linear polymer, non-monotonic behavior might well have been observed in the resulting star-linear blends. Since the data for the $\phi_s=0.2$, 0.4, and 0.6 are already close to each other in Figure S9-A, it seems reasonable that only a modest increase (less than a factor of two) in linear molecular weight might be sufficient to provoke non-monotonic behavior in the data. If so, since the terminal relaxation of the pure 47KS star is at least one magnitude larger than that of the pure 260KL linear, non-monotonicity in a 47KS-linear blend might occur even before the relaxation time of the linear chain exceeds that of the star.

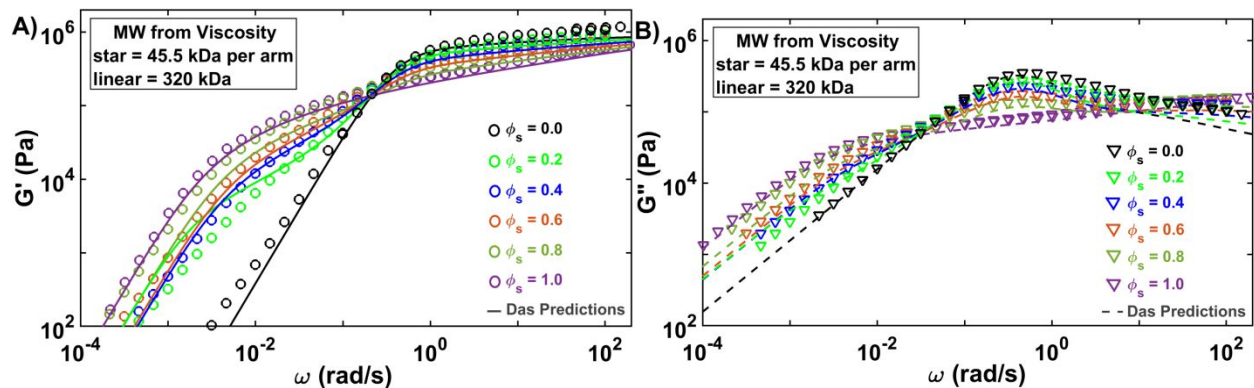


Figure S9: The same as Figure S6, but for the 47KS-260KL blend series.

II.2.ii Predictions using molecular weights measured by GPC

In conjunction with Figures S6-S9, which show Hierarchical model predictions for the ~ 40 KS-linear blend sets using molecular weights estimated through zero-shear viscosity fitting, we report here predictions of the same datasets using the GPC molecular weights. As shown by comparing Figure S10 with Figure S6, model predictions for the 44KS-13.3KL rheology are less accurate with the GPC molecular weights than with molecular weights based on zero-shear viscosity data, given in Table 5 of the main text. In Figure S10-A, the model overpredicts the relaxation time of the pure 44KS by a factor of roughly 3 along the x-axis, while that for the pure 13.3KL is underpredicted by a factor of 2.2. In addition, the relaxation times for $\phi_s=0.9$ and 0.8 blends are overpredicted by roughly factors of 2.3 and 2, respectively. In contrast, model predictions for $\phi_s=0.6, 0.4$ and 0.2 blends are improved in Figure S10 relative to Figure S6. Overall, the use of GPC molecular weights in the Hierarchical model predictions of the 44KS-13.3KL does not contradict the conclusion drawn from Figure S6, that model predictions are in general agreement with the star-linear blend experimental rheology, as long as the terminal relaxation time of the pure star is at least 3-4 orders of magnitude larger than that of the pure linear component.

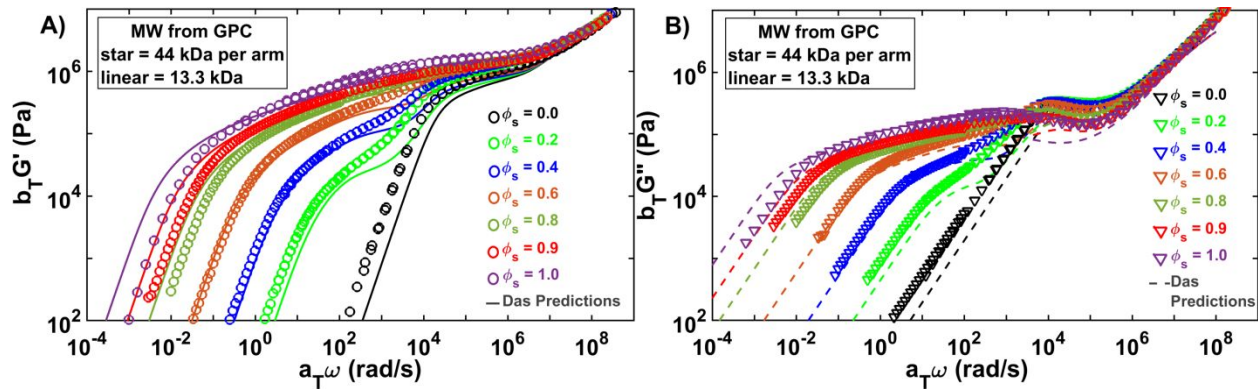


Figure S10: A) G' and B) G'' linear rheology of the 44KS-13.3KL 1,4-polybutadiene star-linear blends with star volume fractions (ϕ_s) 1, 0.9, 0.8, 0.6, 0.4, 0.2 and 0 compared to Hierarchical model predictions (lines) that use the pure star and pure linear molecular weights measured by GPC, given in the legend.

Hierarchical model predictions (lines), using GPC molecular weights, are reasonably successful in predicting the 47KS-73KL rheology data (symbols) shown in Figure S11. Model predictions in Figure S11-A of the 73KL linear polymer do not match as closely the data as do predictions for the same linear molecules in Figure S7, which use the molecular weights from fits to zero-shear viscosity. However, predictions of the 44KS-73KL blends in Figure S11 are overall quite comparable to those in Figure S7. Therefore, as already stated in the discussion concerning Figure S11, the use of GPC molecular weights in the Hierarchical model yields results consistent with the conclusions from predictions based on star and linear molecular weights determined by the zero-shear viscosity.

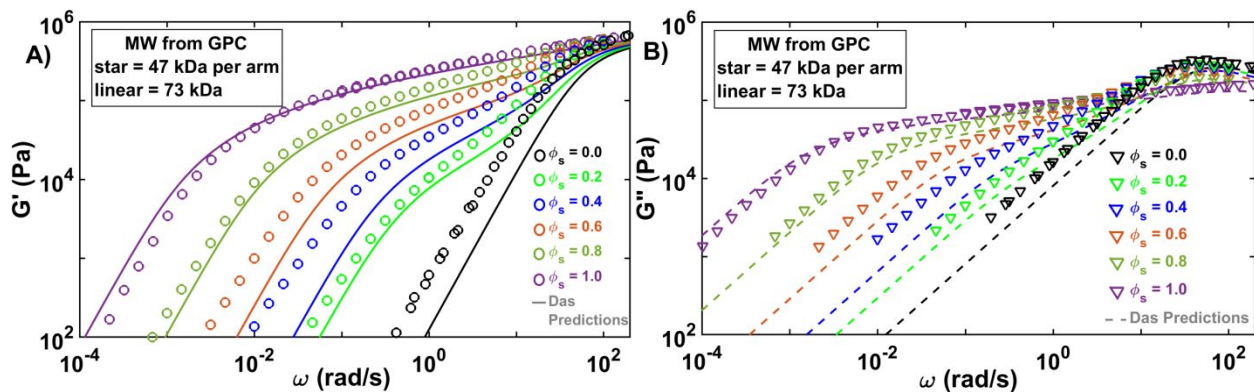


Figure S11: The same as Figure S10, but for 47KS-73KL blends.

Figure S12 shows that using molecular weights given by GPC in the Hierarchical model does not improve the predictions (lines) of the 42.3KS-105KL data (symbols) of Struglinski et al.^[1] As in Figure S8, which compares 42.3KS-105KL data with predictions using molecular weights from zero-shear viscosity (in Table 5 of the main text), predictions in Figure S12 also incorrectly show non-monotonicity of the dependence of terminal relaxation time on ϕ_s . Likewise, in Figure S13, the Hierarchical model with GPC molecular weights predicts 47KS-260KL rheology consistent with that of Figure S9, whose molecular weights are based on zero-shear viscosities.

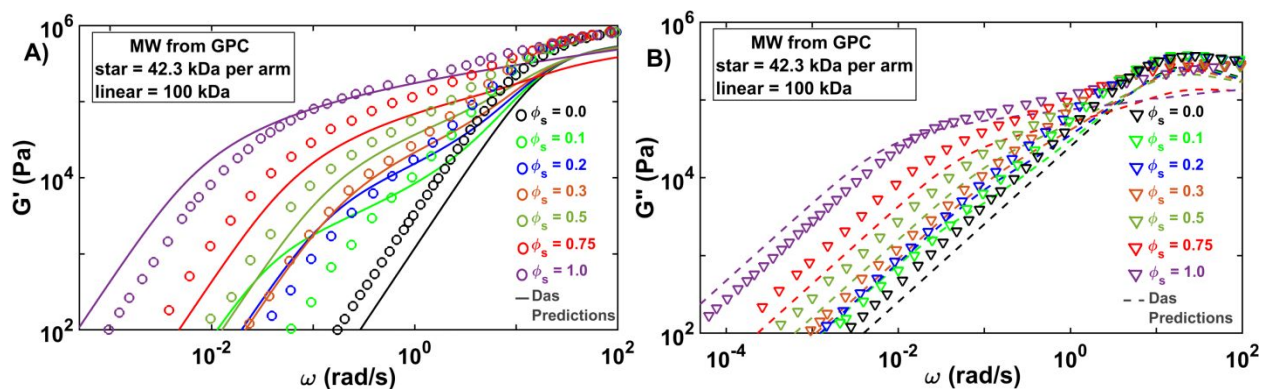


Figure S12: The same as Figure S10, but for 42.3KS-105KL blends taken from Struglinski et al.^[1]

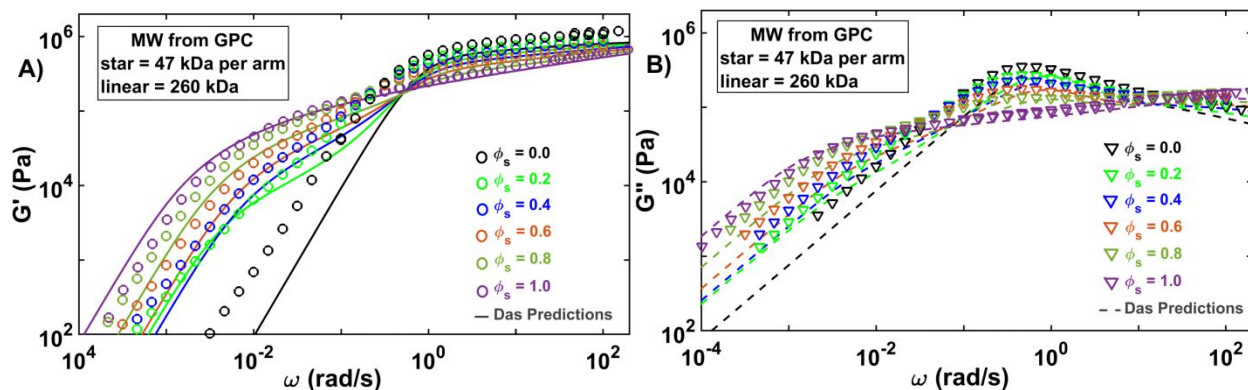


Figure S13: The same as Figure S10, but for 47KS-260KL blends.

II.3 Loss modulus model predictions of the ~20KS-linear blend sets

For completeness, we present here the G'' linear rheology of the ~20KS-linear blend datasets, that correspond with the G' data shown in Figures 10-13 of the main text. Consistent with the main text, the model predictions shown in Figures S14-S18 use molecular weights defined by both zero-shear viscosity fitting and GPC measurements. The G' data are more sensitive than the G'' data to relaxation mechanisms in the terminal regime; thus, please refer to the main text for a thorough discussion of the Hierarchical model's accuracy in predicting the ~20KS-linear blend datasets.

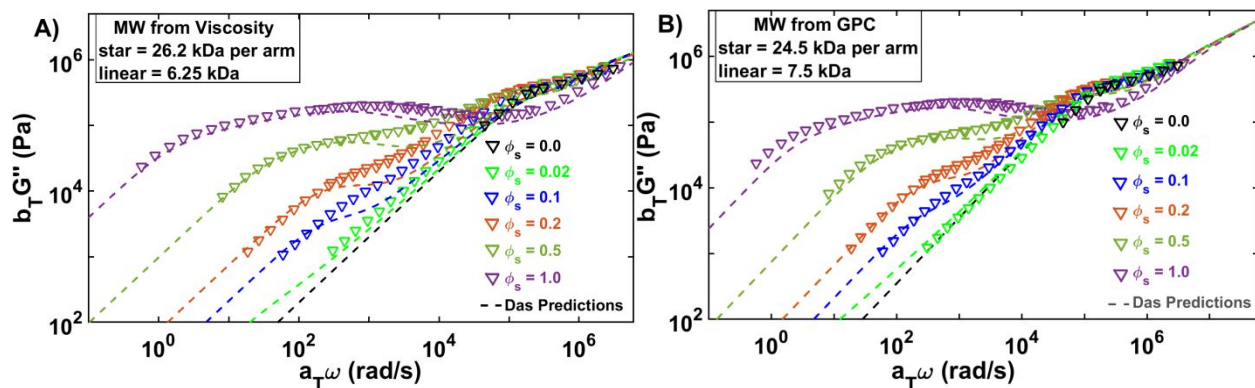


Figure S14: G'' linear rheology of the 24.5KS-7.5KL 1,4-polybutadiene star-linear blends with star volume fractions (ϕ_s) 1, 0.5, 0.2, 0.1, 0.02, and 0, taken from Shivokhin et al.^[6] compared to Hierarchical model predictions (lines) that use the pure star and pure linear molecular weights extracted from A) zero-shear viscosity fitting and from B) GPC. The molecular weights are given in the legend.

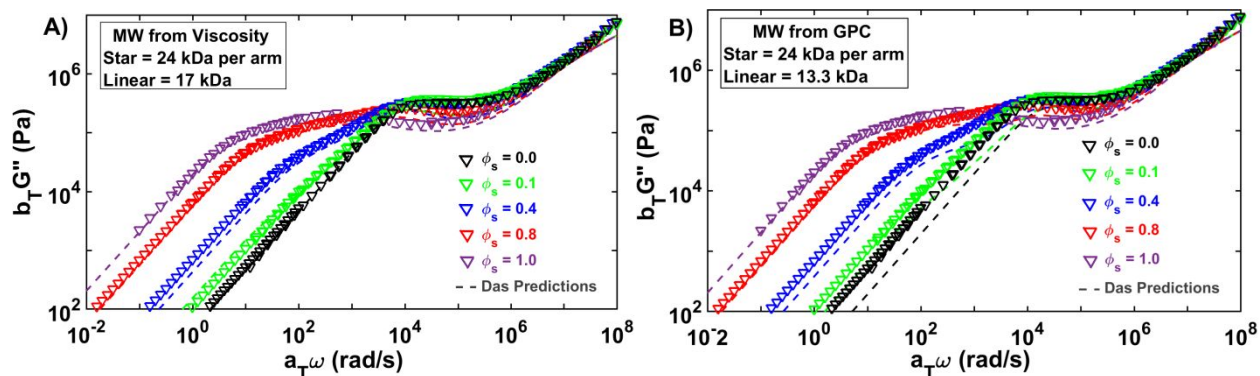


Figure S15: The same as Figure S14, but for the 24KS-13.3KL star-linear blends.

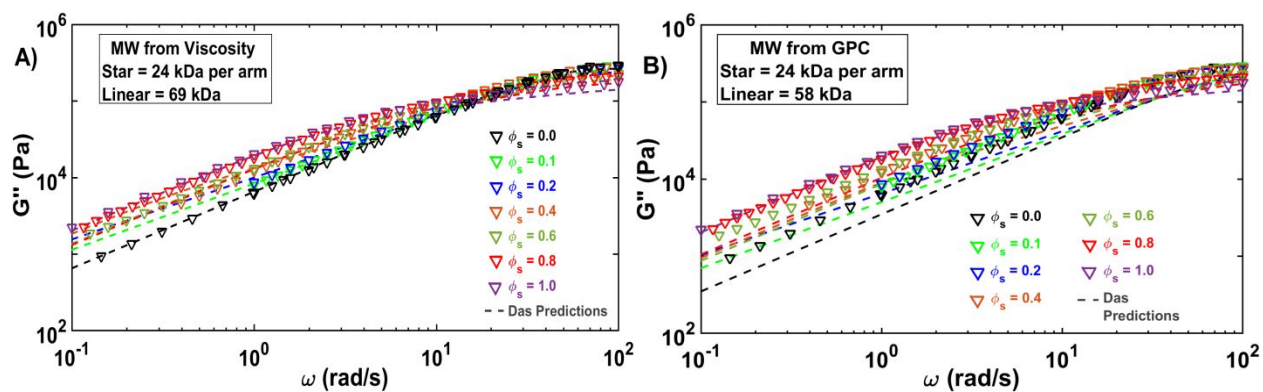


Figure S16: The same as Figure S14, but for the 24KS-58KL star-linear blends taken from Desai et al.^[7]

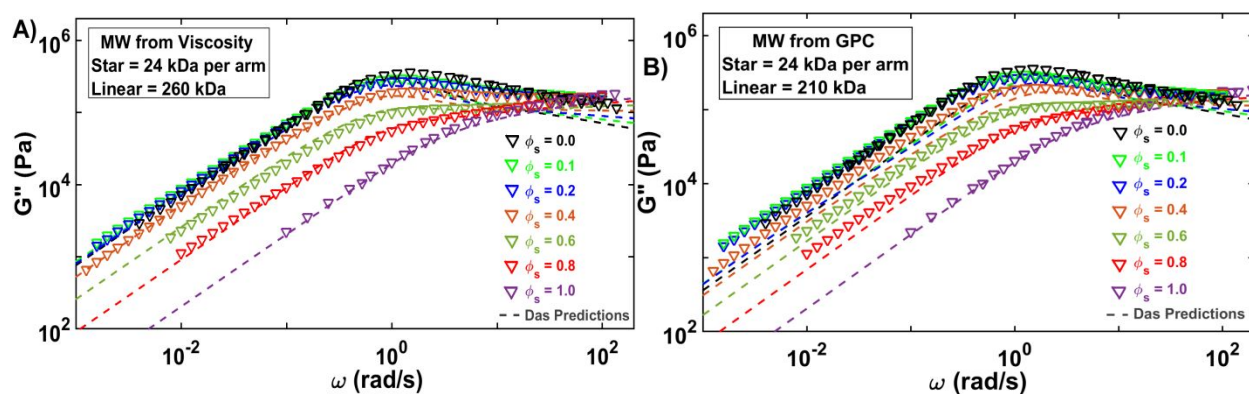


Figure S17: The same as Figure S14, but for the 24KS-210KL blends.

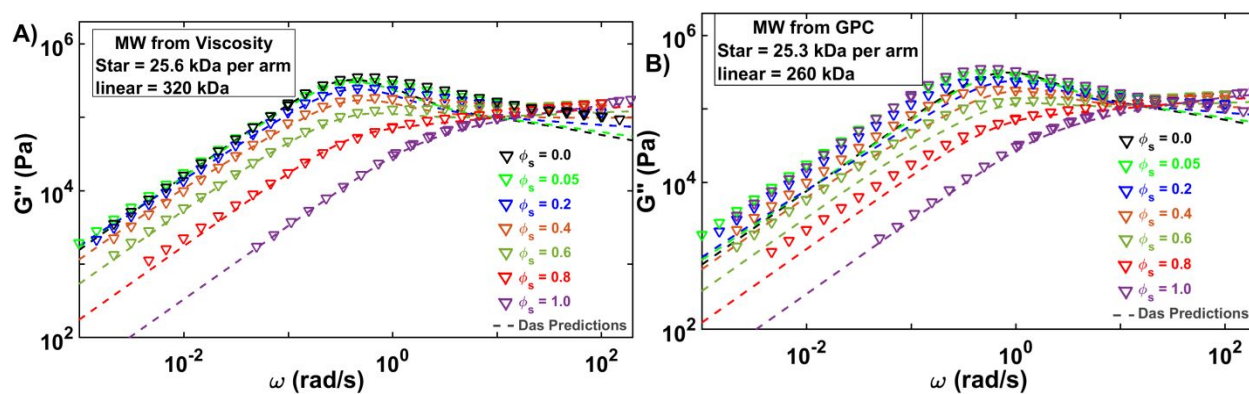


Figure S18: The same as Figure S14, but for the 25.3KS-260KL blends.

II.4 Influence of polydispersity on non-monotonicity

In Figures 13 and 14 of the main text, the 24KS-210KL and 25.3KS-260KL star-linear blends present surprising non-monotonicity, in which the blends have a longer relaxation time than either the pure star or the pure linear polymer. These blends are the first to be studied at multiple star volume fractions in which the pure linear polymer has a somewhat longer relaxation time than the pure star. (There are, however, some polyisoprene blends with 10% star in which the star relaxation time is much shorter than the linear polyisoprene.^[8] These were studied to assess the case in which the linear polymer is considered to be a “fixed matrix” in which the dilute star polymer relaxes. Since these studies did not encompass multiple star volume fractions, non-monotonicity of the kind considered here could not be observed.) However, the pure 210KL and pure 260KL linear polymers in these blends show in their terminal relaxation evidence of some polydispersity. It is worth considering if this polydispersity could potentially contribute to, or be entirely responsible for, the observed non-monotonicity in the rheology of the 24KS-210KL and 25.3KS-260KL blends.

We therefore here investigate the impact of this polydispersity on the non-monotonic behavior of the blends by first fitting the pure 210KL (symbols) and 260KL (symbols) with Hierarchical model predictions (pink lines) which accommodate polydispersity, shown respectively in Figures S19 and S20. As a reference, we include the initial Hierarchical model predictions (green lines) that utilize the molecular weights from Table 5 in the main text. The pink lines, which are model predictions with polydispersity identified through model fitting,

superpose better with the 210KL and 260KL melts. The polydispersity in the pure 210KL is captured with a binary linear blend of 260 kDa (95% volume) and 500 kDa (5% volume), whereas the 260KL is also modeled by a binary linear blend of a 320 kDa (95% volume) and a 560 kDa linear chain (5% volume).

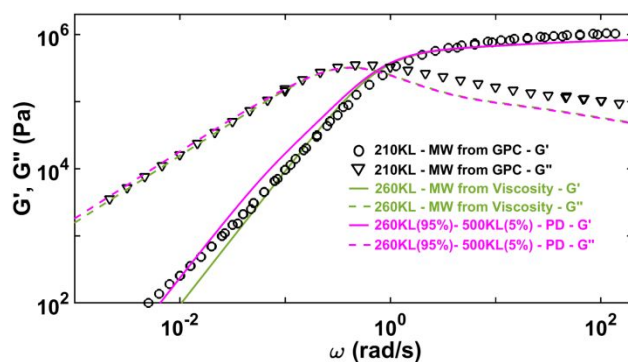


Figure S19: Linear rheology of the pure 210KL melt (symbols) compared with Hierarchical model predictions (lines). The pink lines are model fits using 2-component polydispersity “PD” in the pure 210KL melt, as discussed in the text of the SI, while the green lines are for a single-component linear with molecular weight taken from Table 5 of the main text.

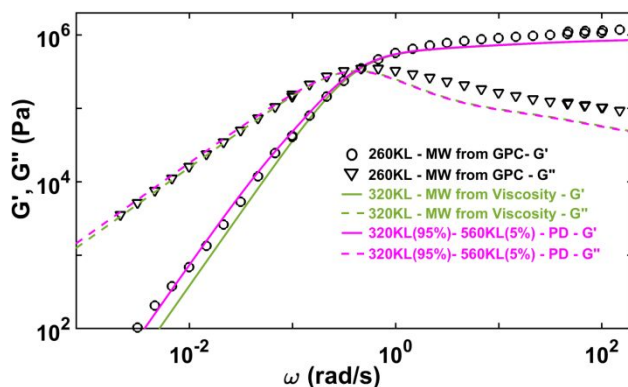


Figure S20: The same as Figure S19, but for the pure 260KL 1,4-polybutadiene melt.

After modeling the polydispersities of the pure 210KL and 260KL polymers with the Hierarchical model, we generated model predictions (lines) to compare with the data (symbols) for the 24KS-210KL and the 25.3KS-260KL star-linear blends, shown respectively in Figures S21 and S22. Although accounting for polydispersity, the model continues to predict non-monotonicity in the 24KS-210KL and 25.3KS-260KL blends and gives reasonable agreement with each blend composition. Thus, it is unlikely that the non-monotonicity in the dependence of relaxation time on blend composition is a result of the slight polydispersity in the pure 210KL and pure 260KL melts.

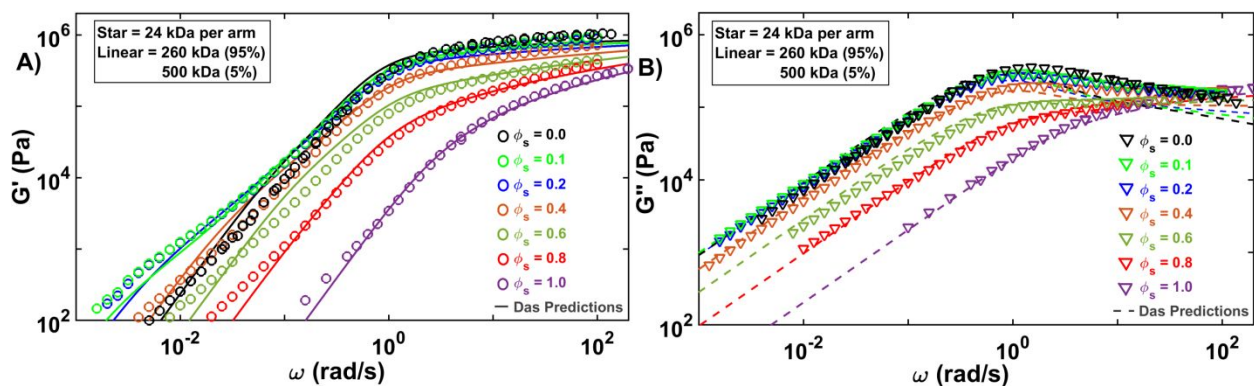


Figure S21: A) G' and B) G'' of the 24KS-210KL blends (symbols), compared with Hierarchical model predictions (lines) using the polydispersity obtained by the fits in Figure S19, and listed in the legend.

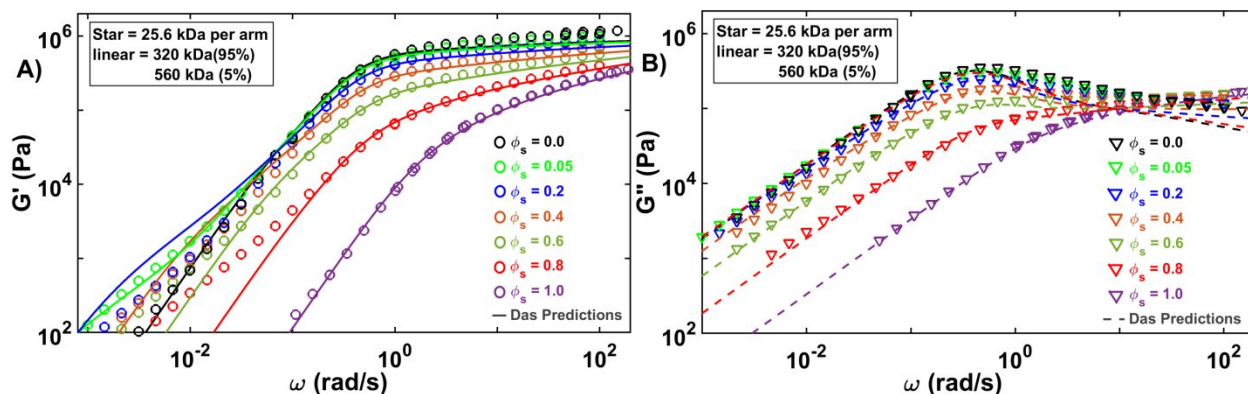


Figure S22: The same as Figure S21, but for the 25.3KS-260KL blends with polydispersity determined by the fits in Figure S20.

II.5 Comparison of star-linear predictions of the BoB and the Hierarchical models

In the Theoretical Modeling section of the main text, we stated that predictions of the Hierarchical model, using the Das parameters and thin tube CR-Rouse, are similar to predictions of the Branch-on-Branch (BoB) model, which originates from the work of Das et al.^[2] Here in Figure S23, we demonstrate this by comparing the Hierarchical model and BoB model predictions (lines) for the 25.3KS-260KL star-linear blend series (symbols), which is one of the blend series that show non-monotonic relaxation. The molecular weights of the pure star and pure linear utilized in both Hierarchical and BoB model predictions are based on fits to the experimental viscosities, and are given in Table 5 in the main text. Figure S23 shows no significant difference between predictions of the BoB and Hierarchical models.

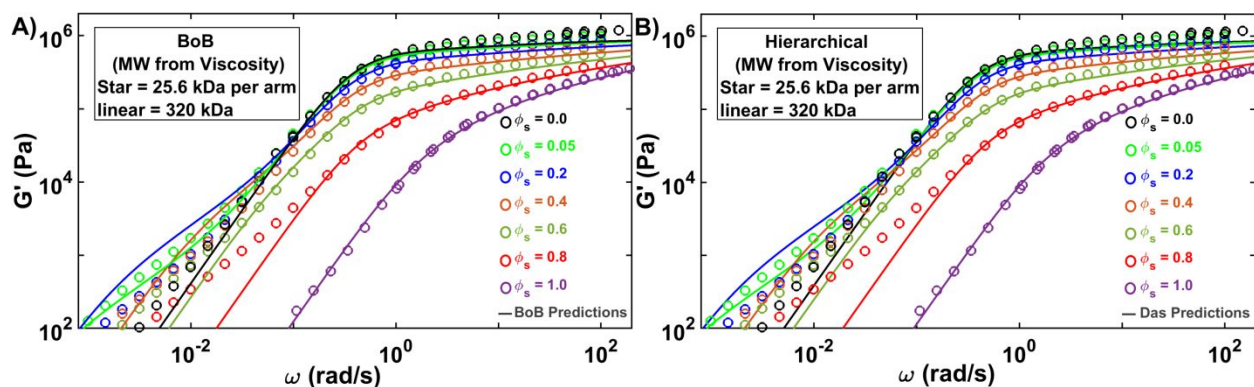


Figure S23: Predictions of A) Branch-on-Branch (BoB) model^[2] and B) Hierarchical model, for 25.3KS-260KL blend series, where symbols are experimental data and the molecular weights of the pure components are based on their viscosities.

II.6 Clarifying model predictions of non-monotonicity of star-linear blends

In Figures 8 and 15 of the main text, we introduced the 25.3KS-73KL blend series to assess further the onset of non-monotonic relaxation time dependence on star volume fraction (ϕ_s) in the experimental data. This blend series corresponds to a case in which the terminal relaxation frequency of the pure linear polymer is shorter than, but separated by less than one order of magnitude, from the pure star. As shown in Figure 8 of the main text, the 25.3KS-73KL blends did not yield non-monotonic behavior experimentally, although non-monotonic behavior was predicted by the Hierarchical model. Here we supplement Figure 8 by providing the linear rheology data of the 25.3KS-73KL blends, as shown in Figures S24 and S25. Figure S24 compares experimental data (symbols) with Hierarchical model predictions (lines) that utilize star and linear molecular weights obtained from fitting the zero-shear viscosity, while in Figure S25 the star and linear molecular weights were measured by GPC.

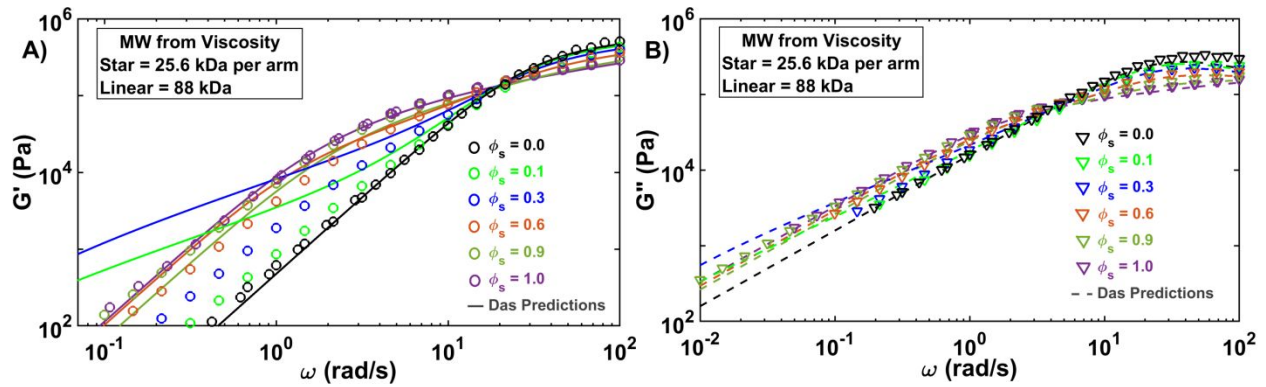


Figure S24: Experimental (symbols) A) G' and B) G'' linear rheology data of the 25.3KS-73KL blends series, for star volume fractions (ϕ_s) 0, 0.1, 0.3, 0.6, 0.9 and 1, compared with predictions of the Hierarchical model using molecular weights obtained from zero-shear viscosity fitting.

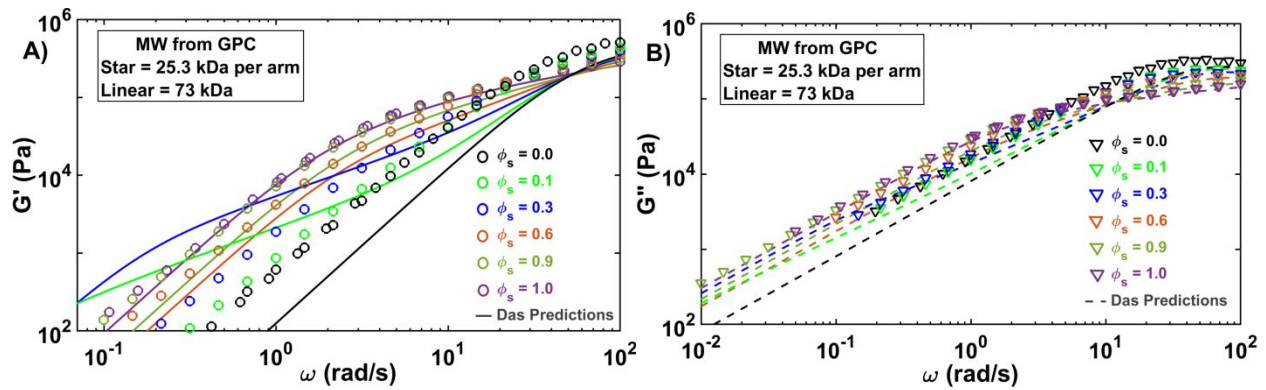


Figure S25: The same as Figure S24, but using molecular weights from GPC.

II.7 Model predictions of star-linear blends using CR-Rouse “fat tube” relaxation

To supplement the Hierarchical model predictions of star-linear blend datasets that assume the Constraint Release-Rouse “thin tube” option, as shown throughout the main text and in previous sections of the Supplemental Information, we present here model predictions using the CR-Rouse “fat tube” option for select star-linear blends in Figures S26-S28. We perform this assessment to uncover how an alternative constraint release assumption may impact the predicted non-monotonicity, or lack thereof, for the 24KS-7.5KL blends taken from Shivokhin et. al.^[6] and the freshly prepared 24KS-210KL and 25.3KS-260KL blends. Consistent with model predictions shown in the main text and in previous sections of this document, we will also continue to use “Das” parameter set, which sets the dilution exponent (α) to unity. In addition, the predictions here will also use molecular weights obtained from zero-shear viscosity fitting and from GPC measurements.

Consistent with model predictions that use the CR-Rouse “thin tube” option in Figure 10 of the main text, the “fat tube” option also yields monotonic predictions that agrees well with the Shivokhin et al.^[6] 24KS-7.5KL blends shown in Figure S26. The similarity in predictions of the two CR-Rouse options for this star-linear dataset is possibly correlated with the fact that the pure 24KS is at least four orders of magnitude slower in relaxation time than the pure 7.5KL.

However, the sensitivity of model predictions on the CR-Rouse assumption becomes apparent for the 24KS-210KL and the 25.3KS-260KL blends, which show non-monotonicity in the dependence of their terminal relaxation time on blend composition. Although the CR-Rouse “fat tube” option correctly predicts the non-monotonicity, as shown respectively in Figures S26 and S27, these predictions do not superpose well with the datasets. Model predictions using

the “thin tube” option are considerably more successful in capturing the rheology of the 24KS-210KL and 25.3KS-260KL blends shown in Figures 13 and 14 of the main text, respectively.

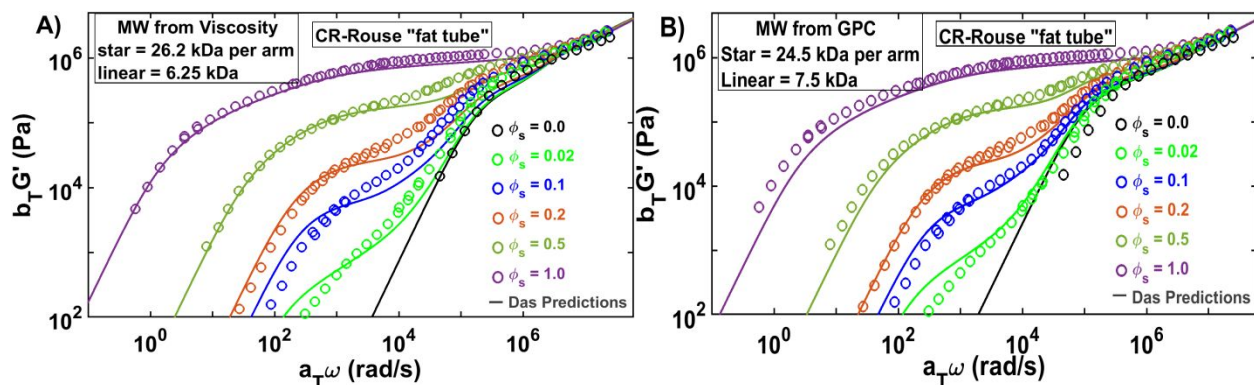


Figure S26: G' linear rheology of the 24.5KS-7.5KL 1,4-polybutadiene star-linear blends with star volume fractions (ϕ_s) 1, 0.5, 0.2, 0.1, 0.02, and 0, taken from Shivokhin et al.^[6] compared to Hierarchical model predictions (lines) that use the pure star and pure linear molecular weights extracted from A) zero-shear viscosity fitting and B) GPC, as given in the legend. Model predictions use the Constraint Release-Rouse (CR-Rouse) “fat tube” and a dilution exponent (α) of unity.

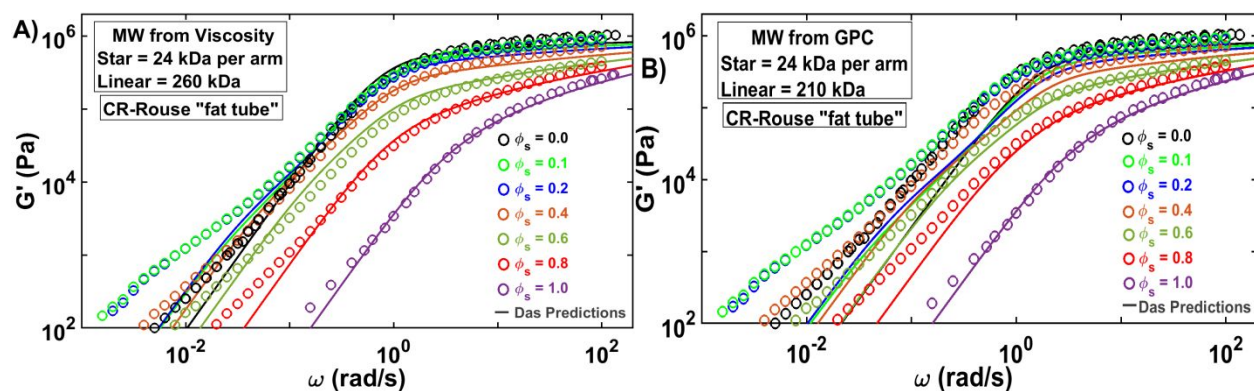


Figure S27: The same as Figure S26, but for the 24KS-210KL blends.

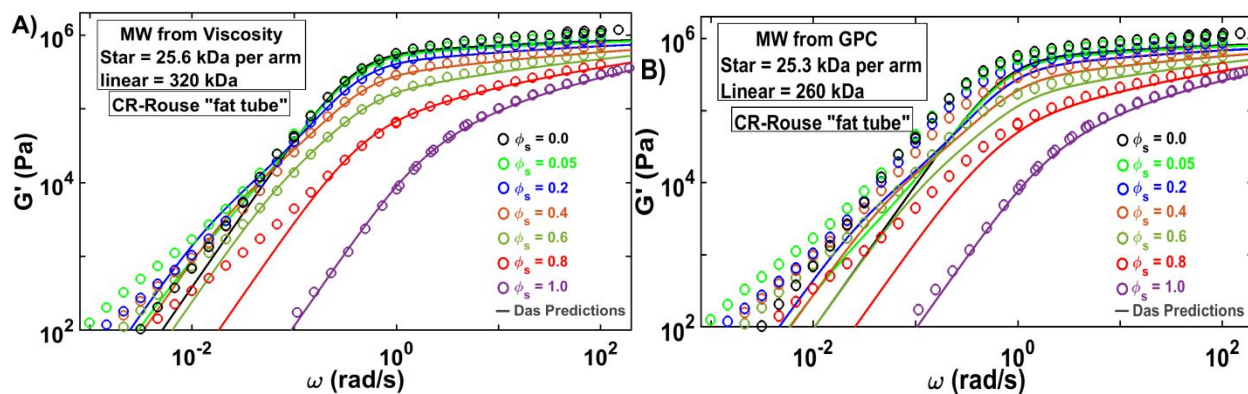
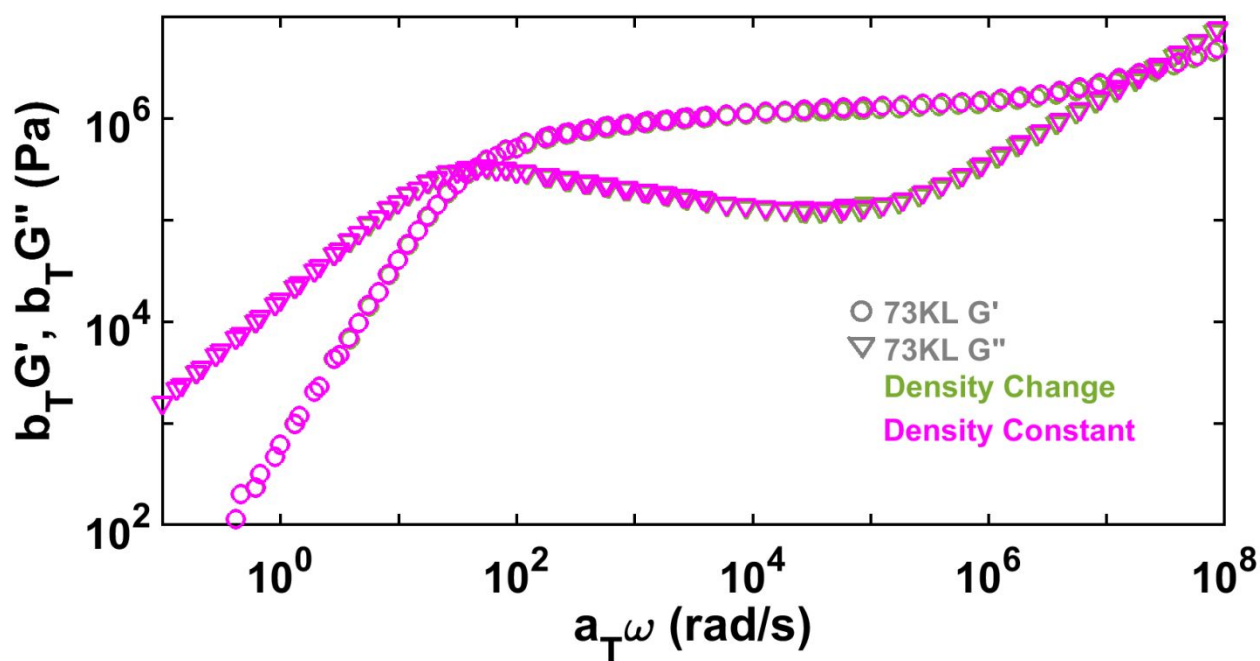


Figure S28: The same as Figure S26, but for the 25.3KS-260KL blends.

II.8 Master curves generated with and without temperature-dependent density.

Most of our master curves were generated using vertical shifts proportional to absolute temperature but ignoring density changes with temperature, which were at most around 7% at the lowest temperature. The effect of including the density variation is shown in the typical master curve in Figure S29.



73KL pure – Density Change			
Temp (Celsius)	Temp (Kelvin)	Vertical Shift Factor	Density (g/cm ³)
-85.025238	187.974762	1.4910436	1.063227811
-75.016449	197.983551	1.4126571	1.065492381
-50.003677	222.996323	1.2855734	1.039493157
-24.994654	248.005346	1.1714978	1.025684269
24.999966	297.999966	1	1

73KL pure – Density Constant			
Temp (Celsius)	Temp (Kelvin)	Vertical Shift Factor	Density (g/cm ³)
-85.025238	187.974762	1.5849476	1.000234344
-75.016449	197.983551	1.5048834	1.00019402
-50.003677	222.996323	1.3361989	1.000109155
-24.994654	248.005346	1.2015373	1.000041251
24.999966	297.999966	1	1

Figure S29. Comparison of master curves obtained using variation of density with temperature and ignoring this variation, shown in green and pink respectively. The vertical shift factors computed with the rheometer “Orchestrator” software are given.

III. REFERENCES

- [1] Struglinski, M. J.; Graessley, W. W.; Fetters, L. J. Effects of Polydispersity on the Linear Viscoelastic Properties of Entangled Polymers. 3. Experimental Observations on Binary Mixtures of Linear and Star Polybutadienes. *Macromolecules* **1988**, 21, 783–789.
- [2] Das, C.; Inkson, N. J.; Read, D. J.; Kelmanson, M. A.; McLeish, T. C. B. Computational Linear Rheology of General Branch-on-Branch Polymers. *J. Rheol.* **2006**, 50 (2), 207–234.
- [3] Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. Anionic polymerization: High vacuum techniques. *J. Polym Sci A: Polym. Chem.* **2000**, 38, 3211.
- [4] Hadjichristidis, N.; Roovers, J. Linear viscoelastic properties of mixtures of 3- and 4-arm polybutadiene stars. *Polymer*, **1985**, 26, 1087
- [5] Polymeropoulos, G.; Zapsas, G.; Ntetsikas, K.; Bilalis, P.; Gnanou, Y.; Hadjichristidis, N. 50th Anniversary Perspective: Polymers with complex architectures. *Macromolecules* **2017**, 50, 1253.
- [6] Shivokhin, M. E.; van Ruymbeke, E.; Bailly, C.; Kouloumasis, D.; Hadjichristidis, N.; Likhtman, A. E. Understanding Constraint Release in Star/Linear Polymer Blends. *Macromolecules* **2014**, 47 (7), 2451–2463.

[7] Desai, P.S.; Kang, B.G.; Katzarova, M.; Hall, R.; Huang, Q.; Lee, S.; Shivokhin, M.; Chang, T.; Venerus, D.C.; Mays, J.; Schieber, J.D.; and Larson, R.G. Challenging Tube and Slip-Link Models: Predicting the Linear Rheology of Blends of Well-Characterized Star and Linear 1,4-Polybutadienes. *Macromolecules* **2016**, 49(13), 4964-4977

[8] Matsumiya, Y.; Masubuchi, Y.; Inoue, T.; Urakawa, O.; Liu, C.; van Ruymbeke, E.; Watanabe, H. Dielectric and Viscoelastic Behavior of Star-Branched Polyisoprene: Two Coarse-Grained Length Scales in Dynamic Tube Dilation. *Macromolecules* **2014**, 47(21), 7637–7652