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Synthesis, Hydrogenation, and Rheology of 1,2-Polybutadiene Star Polymers

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ABSTRACT: A series of symmetric star polymer melts were synthesized with arm molecular weights varying between 10 000 and 80 000 g mol^{-1}. Each sample had a three-arm architecture and was predominately made up of 1,2 enchained polybutadiene repeat units. A portion of each sample was hydrogenated to give the corresponding poly(1-butene) material. Mechanical analysis was carried out on both the parents and saturated analogues. Results obtained from these rheological investigations were compared to theoretical predictions calculated using the Milner−McLeish theory and found to agree well over the frequency range employed, for both "parent" and "daughter" products.

Introduction

A large number of well-defined polymer materials have been extensively studied with respect to their viscoelastic behavior. The response of a polymer material to an applied stress varies in relation to several factors including the chemistry of the polymer chain, its molecular weight, and the amount of chain branching.

The viscoelastic spectra of entangled star polymer melts measured over a wide range of frequency indicate very long relaxation times. The de Gennes' tube model[2] of a melt envisages every chain as confined by its neighbors to a "tube" along which it can diffuse (reptate) by curvilinear motion. In the case of branched polymers, of which the symmetric three-armed stars described here are the most simple example, such movement of the branch point necessitates the entry of two arms into the neighboring part of the tube hitherto occupied by the third arm. In consequence, the branch points become trapped in the entanglement network, confining the relaxation dynamics to exponentially unlikely fluctuation modes; hence the long time scales. The tube model predicts that the viscoelastic spectrum depends only on the molecular weight of each arm and not on the total molecular weight of the polymer.

Previously, a number of studies, using well-defined polymer samples, have been undertaken in order to test the validity of the theories designed to predict viscoelastic behavior in polymers. These have encompassed both differing chemistry and microstructures and various architectures. In many cases they consist of polydiene species produced anionically. This technique provides several advantages over other polymerization methods, in that the polymers produced have narrow polydispersities (typically around 1.05−1.15) and controlled microstructures and (provided the "living" anionic chain end is preserved after polymerization is complete) allow the construction of precise architectures such as stars[3−6] and H-shaped[7] species via linking of chains with chlorosilane compounds.

Milner and McLeish[1] proposed a detailed tube theory for star polymer viscoelasticity, associating stress relaxation with diffusion of the chain end along a tube that dilates dynamically as the relaxation progresses. Their theory has proved quantitatively accurate for polyisoprenes and 1,4-polybutadienes.[1,8,9] Generalizations have been proposed for blends of star polymers with other topologies[10,11] and for higher-order branching structures.[12,13] However, it has recently been suggested[42] that the dynamic tube dilation picture is not valid at long times, despite the apparent success in matching the linear viscoelastic data. We examine the Milner−McLeish theory with a series of 1,2-polybutadiene star polymers, before and after hydrogenation. This provides an important new test of the theory, which has not yet been applied to these chemistries or to the simultaneous prediction of the rheological behavior of both "parent" and "daughter" polymer series produced by hydrogenation.

Another motivation for the systematic exploration of star polymers of various architectures, especially their hydrogenated variants, is the record of departures from universal behavior.[14−16] Several, usually saturated architectures have shown "thermorheological complexity". In one case,[16] optimized fitting to the tube model theory required setting a value for the entanglement molecular weight, M_e, different from that obtained by the plateau modulus.

The microstructure of polybutadiene and other polydienes produced anionically using organolithium initiators can be varied at will by changes in reaction conditions.[17,18] If carried out in a nonpolar solvent such as *n*-hexane at ambient temperature, a product with about 94% 1,4-enchainment typically results. Conversely polar solvents or additives and low reaction temperatures favor vinyl addition. One such polar additive, 1,2-dipiperidinoethane (DIPIP), has been shown[17,19] to be particularly effective with regards microstructure control, resulting in 100% 1,2-enchainment at relatively low ratios of [DIPIP]:[Li] in nonpolar solvents such as *n*-hexane. However, in the present study, attempts to link chains synthesized in the presence of DIPIP to form stars met with only limited success, and this route was abandoned. Polymerization

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in a polar solvent, in this case THF at relatively low reaction temperatures, presented fewer problems and enabled the production of symmetric three-armed stars having 85−90% 1,2-enchainment, which allowed valid comparisons between theoretical and experimental rheology to be drawn.

Milner−McLeish Theory

Stress in entangled star polymers relaxes by fluctuations of the star arms. The tube model[20] predicts that the branch point prevents reptation and consequently that fluctuation in the entangled path length dominates the relaxation. Milner and McLeish[1] use the tube model to give a detailed theory of this relaxation. In this section we briefly summarize the theory, before applying it to the star polymers in this study.

The theory uses three parameters to predict the rheology of star polymers across the entire frequency range. These are the plateau modulus G_0, the Rouse time of an entanglement segment τ_e, and the dimensionless entangled path length s of each arm. The path length s is given by the ratio of the molecular mass of the arms to the entanglement molecular weight M_e. Each parameter is fixed by the chemistry of the polymer, independent of the star topology, and may therefore be fixed by experiments on linear polymers.

In the tube model, star relaxation is essentially a one-dimensional diffusion of the free end of the polymer chain along the tube contour. Since the branch point of the star is effectively pinned by the tube surrounding each arm emanating from that point, diffusion of the free end, or retraction of each arm along its tube contour, will inevitably incur an entropic penalty. Fewer configurations of the chain are compatible with a smaller separation between the branch point of the star and the free ends of the arms. Therefore, the polymer chain may be thought of as an entropic spring,[20] so the free-end diffusion occurs in a quadratic potential.

A relaxation time for each point along the star arm is defined as the first passage time for the free end to diffuse to this point.[21] Physically, once the free end has retracted to a given point inside the tube, subsequent motions can explore any configuration. The first passage time, for diffusion in the potential U, is given by[1]

$$\tau(x) = (L^2/D)\int_0^x \mathrm{d}x' \exp\{U(x')/kT\}\int_{-\infty}^{x'} \mathrm{d}x'' \exp\{-U(x'')/kT\} \quad (1)$$

with arm length $L = {}^5/_4 sa$, free-end diffusion coefficient $D = 5a^2/(6\pi^2 s\tau_e)$, and fractional distance from the free end, x.

Ball and McLeish[22] showed how to renormalize the potential to account for the relaxation of surrounding chains. As the relaxation progresses, chains relax and no longer contribute to the stress or the entanglements that form the tube. This “dynamic-dilution” process reduces the energy barrier to the star arm fluctuations to a subquadratic form:

$$\frac{U(x)}{kT} = \frac{15}{4}\,\frac{s(1-(1-x)^{\beta}(1+\beta x))}{\beta(\beta+1)} \quad (2)$$

The value of $\beta = {}^7/_3$ was proposed by Milner and McLeish,[1] following a scaling argument.[23] Dynamic dilution also gives an expression for the modulus

$$G_e(t) = \beta G_0\int_0^1 \mathrm{d}x\,(1-x)^{\beta-1}\exp\{-t/\tau(x)\} \quad (3)$$

At early times, the first $\sim 1/\sqrt{s}$ fraction of chain relaxes via nonactivated retraction using all the Rouse modes of the chain. The result for this small x regime is

$$\tau(x) = (225/256)\pi^3 s^4 x^4 \tau_e \quad (4)$$

with a simple crossover to eq 1 at large x. We follow this technique and solve eq 1 numerically to calculate the dynamic moduli.

At high frequency the polymer follows the Rouse spectrum,[20] which we include to make our calculations cover the full frequency range. Rouse modes longer than an entanglement time are restricted to the one-dimensional tube contour, so their contribution is reduced in modulus by one-third.[24] In contrast, all Rouse modes faster than the entanglement time may be accessed, and therefore we add the following contribution to our moduli:

$$G_R(t) = {}^1/_3 G_0/s\sum_{p=1}^{s-1}\exp\{-p^2 t/\tau_R\} + G_0/s\sum_{p=s}^{\infty}\exp\{-p^2 t/\tau_R\} \quad (5)$$

The Rouse relaxation time is related to the entanglement time via $\tau_R = s^2\tau_e$.

The total stress relaxation modulus, $G(t)$, is given by the sum of the entangled (3) and Rouse (5) contributions. By taking the Fourier transform of $G(t)$, the dynamic moduli are calculated. The storage modulus, G', and the loss modulus, G'', are the real and imaginary parts, respectively. Therefore, with only three parameters, predictions for the moduli may be made across the full frequency range of polymer chain dynamics.

Experimental Section

Synthesis. All parent diene star polymers were synthesized using well-documented high-vacuum anionic techniques.[17,25,26]

All glassware, for reactions and material manipulations, was dried in situ immediately prior to use by evacuation, followed by flaming with a hand-held gas torch until a yellow sodium flame was observed. Polymerization reactors generally consisted of a 500 mL round-bottomed flask, equipped with a central inlet bearing a quickfit socket and a greaseless stopcock, which allowed both distillation into and isolation of the vessel from the vacuum line. Sidearms situated on the reactor were attached to ampules containing initiator and chlorosilane solutions and a sampling vessel in which small quantities of arm could be isolated for analysis prior to the bulk of the polymer being linked.

Butadiene monomer (Aldrich) was purified prior to polymerization by stirring first over a sodium mirror and then over solvent-free *n*-butyllithium (Aldrich) for approximately 30 min at around 0 °C. The purified material was stored under vacuum in a graduated vessel, from which accurate volumes could be transferred to polymerization reactors when required. *n*-Hexane was purified by distillation from an oligostyryllithium solution. Tetrahydrofuran (THF) was distilled immediately prior to use from a reservoir containing sodium/potassium alloy together with a little of the violet dinegative ion of benzophenone which acted as an indicator of perfect dryness. DIPIP (Aldrich) was purified by short path distillation from sodium/potassium alloy into pregraduated ampules equipped with a dome-type break-seal and stored in a refrigerator until required. *s*-Butyllithium (Aldrich) was purified by distillation under high vacuum and dissolved in purified *n*-hexane to form a stock solution of approximately known concentration. Ampules of *s*-butyllithium with known volume were prepared by diluting the stock solution under vacuum in a specially prepared buret apparatus from which sealed ampules containing an accurately known volume could then be prepared. The concentration of ampules prepared in this way was determined by titration of the hydrolyzed contents of one or two selected ampules with standard hydrochloric acid solution.

Initially, high vinyl content samples were prepared at ambient temperature in *n*-hexane, to which an approximately 10-fold excess of DIPIP[17,19] based on initiator concentration had been added. This resulted in near-monodisperse polybutadiene arms with a typical 1,2-enchainment (by ^1H NMR) of greater than 92%. Attempts were then made to link three of these "living" arms centrally using methyl trichlorosilane.[27] Several attempts proved unsuccessful, with large quantities of both unlinked arms and two-armed material remaining after reaction times extending up to 14 days. This might be as a consequence of a number of factors:

(a) The bulkiness of the lithium ion−DIPIP complex might prevent the approach of the anionic chain end to the chlorosilane linking agent. This is thought unlikely to be a significant factor because the complexed end must be in equilibrium with the uncomplexed one in order for propagation to take place.

(b) It is possible that cyclization involving the anionic chain end and the contiguous pendant vinyl group may also take place. This has been reported previously[28,29] in anionic polymerization of butadiene, particularly under conditions of monomer starvation, with up to 42% of all monomer being enchained as cyclic units along the backbone reported in the presence of polar modifiers. Such low monomer concentration conditions must also occur toward the end of the polymerization here. Such cyclic structures on the end of the polymer chain may again present a steric barrier to multiarm linking.

(c) Finally, reports[38,39] suggest there is a likelihood that the living anionic chain end may attack ligands such as DIPIP, causing the premature death of the "living" polymer chain before linking to the complete star can take place.

Another route to create the predominantly 1,2 microstructure was required. Several articles[19,30−32] have reported that the use of polar solvents such as tetrahydrofuran (THF) combined with low reaction temperatures gives a high degree of 1,2 microstructure in anionic butadiene polymerization. Accordingly, polybutadienyllithium was prepared by polymerization using THF as the solvent, at between −20 and −30 °C (without DIPIP). Because of the decrease in reaction temperature, the reaction time for the polymerization stage was extended to 72 h, after which the reactor contents were allowed to warm to ambient temperature before addition of the methyltrichlorosilane linking agent. This process gave a considerably improved conversion to the required three-armed star architecture. The ratio of star to unlinked arm prior to fractionation was approximately 40:1 based on GPC peak areas (see Figure 1). Subsequent purification by fractional precipitation from a toluene solution by methanol improved this peak ratio to more than 100:1. Analysis by ^1H NMR revealed a 1,2 microstructure content of between 85 and 90%, and data for the subsequent series of star polymers produced using this technique are given in Table 1.

Hydrogenation. Each sample of purified star was divided into two portions, one of which was hydrogenated to give the corresponding poly(1-butene) star. A homogeneous technique[33,34] involving the thermolysis of tosyl hydrazide to produce the hydrogenating species diimide N_2H_2 in situ was chosen. Addition of a high boiling point base (tri-*n*-propylamine) to the solvent (*o*-xylene) was made in order to prevent the addition of sulfinic acid groups to the polymer backbone.[35] The progress of hydrogenation was monitored via FTIR spectroscopy, and a quantitative analysis was performed by high-temperature (80 °C) ^1H NMR in toluene-d_8 on the final product. In all samples less than 2% of the double bonds present in the original polymer were found to be unsaturated following the process described above. A final comparison of GPC results, both pre- and post-hydrogenation from the 97 600 g mol^{-1} three-arm star material, revealed no evidence of arm cleavage or significant changes in molecular weight (Figure 1). Similar results were obtained for the other star syntheses.

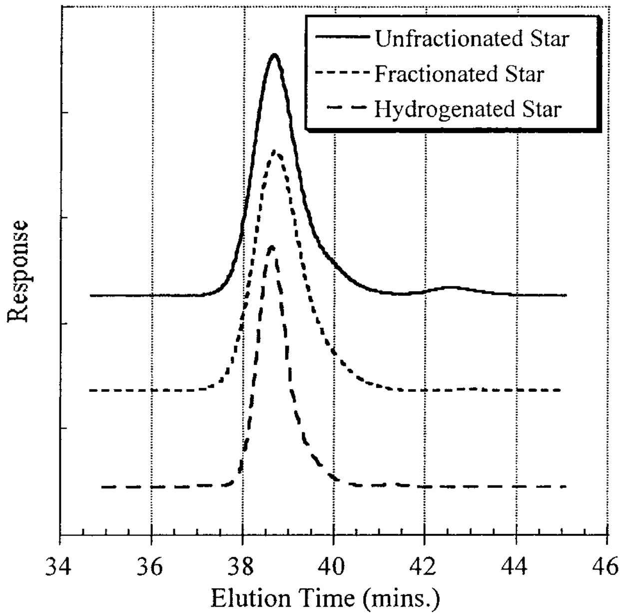

Figure 1. GPC analysis illustrating molecular weight distributions in both pre- and postfractionated 97 600 g mol^{-1} 1,2-polybutadiene three-armed star material.

Table 1. Characterization Results for Three-Arm 1,2-Polybutadiene Stars

arm mol wt (g mol^{-1})	arm PD	star mol wt (g mol^{-1})[a]	star PD	microstructure by ^1H NMR % 1,2	ethyl branches per 1000 backbone carbons
11 300	1.02	30 600	1.01	88.9	400
24 100	1.02	60 800	1.01	88.0	393
38 900	1.01	97 600	1.02	87.4	388
78 600	1.01	203 300	1.04	89.4	404

[a] Star molecular weights appear lower than predicted by corresponding arm molecular weights, due to the proportional reduction of radius of gyration caused by long chain branching in stars, a factor not allowed for when calibrating the GPC with linear standards.

Rheology. The mechanical response to stress of both the unsaturated and hydrogenated samples was investigated using a Rheometrics SR-5000 mechanical spectrometer. Each polymer was first formed into a 25 mm diameter disk with a thickness of between 0.5 and 1.5 mm. The storage and loss moduli of each sample were then determined at a fixed strain of 0.3% (which had previously been found to be well within the linear strain response regime) over a range of frequencies between 0.1 and 100 rad s^{-1} at a number of temperatures. Temperature ranges employed were usually between 10 and 80 °C for the 1,2-polybutadiene samples and −10 and 80 °C for the poly(1-butene), with typically 10 °C steps between individual frequency sweeps. Time−temperature superposition was then used to construct a master curve with 333 K as the reference temperature from data sets collected at various temperatures.

Results and Discussion

Figures 2 and 3 show the time−temperature superposed dynamic moduli for the range of star polymers in this study. We found no evidence for thermorheological complexity, using a single set of WLF parameters for all frequency shifts with a given species. Frequency shift

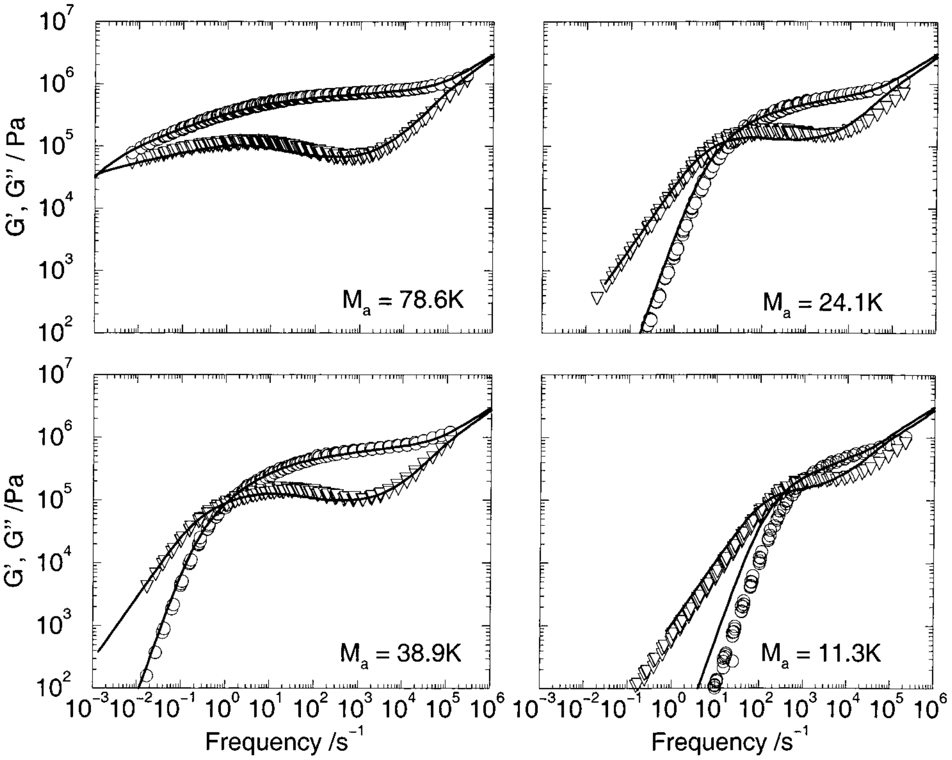

Figure 2. Storage and loss moduli for the three-arm 1,2-polybutadiene star polymers. Curves were calculated using Milner–McLeish Theory[2] with parameters consistent with those for linear polymers.

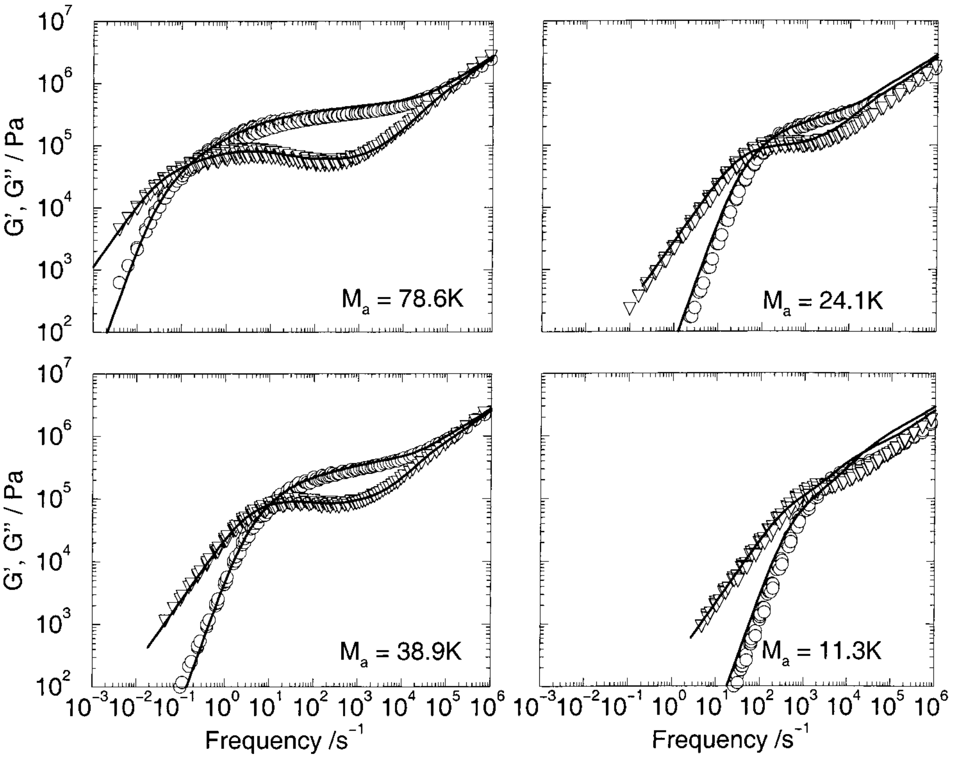

Figure 3. Storage and loss moduli for the three-arm hydrogenated 1,2-polybutadiene star polymers. Curves were calculated using Milner–McLeish theory.[1] Parameters M_e, G_0, and τ_e were chosen to fit the data for the highest molecular weight.

factors a_T were found to follow the WLF equation

$$\log a_T = -C_1(T - T_0)/(C_2 + T - T_0)$$

with $C_1 = 5.83$ and $C_2 = 138.0$ for 1,2-polybutadiene and $C_1 = 8.30$ and $C_2 = 220.0$ for the hydrogenated derivative, for a reference temperature $T_0 = 333$ K. This is consistent with Carella et al.'s[15] observations for hydrogenated linear polybutadiene with a high degree of 1,2-enchainment.

The high molecular weight polymers show a broad spectrum, characteristic of well-entangled star polymers, and we proceeded to compare the data with the Milner–McLeish theory. A literature value[36] of M_e =

Table 2. Parameters Used for the Calculation of Dynamic Moduli of Star Polymers at 333 K

species	M_e/g mol^{-1}	G_0/MPa	τ_e/s
1,2-polybutadiene	3550[a]	0.765	1.02×10^{-5}
poly(1-butene)	6100	0.510	2.04×10^{-5}

[a] Value taken from Ferry.[36]

3550 g mol^{-1} was used for the 1,2-polybutadiene stars, with the experimental arm molecular weights. Theory curves were fitted to the data using parameters τ_e and G_0 extracted from the data on the highest molecular weight polymer as follows. The plateau modulus was obtained from the experimental G' in the rubber zone, and the entanglement time τ_e was found from the intersection between the G_0 line and the Rouse relaxations of slope $^1/_2$. Values of these parameters are given in Table 2 and are within a factor of 1.5 of the published values[36] of $G_0 = 6.2 \times 10^5$ Pa and $\tau_e = 1.7 \times 10^{-5}$ s. [The value of the entanglement time was obtained using $\tau_e = \zeta_0 N_e{}^2 b^2/3\pi^2 kT$, with the values of the monomeric fraction coefficient, ζ_0, and step length, b, tabulated in Ferry's book.[36] The number of monomers in an entanglement length is given by $N_e = M_e/M_0$, with monomeric mass $M_0 = 54$ for polybutadiene.] These values of G_0 and τ_e were then used to obtain theory curves for the remaining molecular masses.

Comparison between the theory and data from the hydrogenated samples was approached in a slightly different way, since no literature value of M_e is available for the exact microstructure. Values of G_0 and τ_e were extracted from the data as above, and the entanglement molecular weight treated as a free parameter. Again, the fitted parameters are shown in Table 2. The best-fit value of the entanglement molecular weight, M_e, was 6100 g mol^{-1}, which is significantly lower than the value of 9536 g mol^{-1} reported by Fetters et al.[37] for 98% 1,2-enchained polybutadiene. This may be due to differences in the microstructure,[18] with around 10% less 1,2-enchainment in this study. A significant decrease may be expected since hydrogenated 1,4-polybutadiene has a much smaller M_e of around 828 g mol^{-1}. Our fitted value is smaller than a simple linear relationship between M_e and the fraction of 1,2-enchainment, which is to be expected since the entanglement molecular weight is proportional to the cube of the packing length.[40]

For a consistency check, we compared the best-fit values for the plateau modulus and entanglement molecular weight. These parameters were fitted independently for the samples yet should be related by

$$G_0 = \rho RT/M_e \tag{6}$$

Our fitted values of G_0 and M_e are consistent with a density of 1.0 g cm^{-3} for both hydrogenated and parent species. This is larger than the actual density[18] of the polymer melts by a factor of about 1.2. However, we note that this discrepancy is less than the variation between the fitted and literature values of G_0. It is also much lower than the factor of 2 that Levine and Milner[16] found necessary to model hydrogenated 1,4-polybutadiene.

The tube theory gives reasonable agreement with the data for each molecular weight over the full frequency range. Parent 1,2-polybutadiene polymers (Figure 2) and their hydrogenated variants (Figure 3) are equally well described by the theory. Closest agreement is found for the highest molecular weights. The lower molecular weight polymers show the largest deviation from the data curves. This may be due to the marginal degree of entanglement, with $s = M_a/M_e = 3.2$ for 1,2-polybutadiene or $s = 1.9$ for the hydrogenated samples.

Conclusions

A series of well-defined three-arm star-type polybutadiene molecules were successfully produced with consistently high degrees of 1,2-enchainment of the order of 87−90% and polydispersities of less than 1.05. Each crude polymer was subsequently purified such that essentially monomodal GPC results were obtained. A portion of each species was hydrogenated using a homogeneous diimide method to an extent of about 98%. Finally, rheology was carried out on both the unsaturated and saturated polymer series.

The Milner−McLeish theory for the relaxation of star polymer melts successfully accounts for the rheological behavior of this series of three-arm 1,2-polybutadiene star polymers. The theory, with suitable changes to the parameters, again reproduced the measured dynamic moduli obtained for the hydrogenated materials. High-frequency Rouse modes were included in the calculations, matching the data at high frequencies.

We found no evidence of thermorheological complexity for either 1,2-polybutadiene or its hydrogenated variant, in contrast to a previous study on hydrogenated 1,4-polybutadiene by Levine and Milner.[16] This observation must be related to the different microstructures in 1,2- and 1,4-enchainment. Levine and Milner[16] suggest that thermorheological complexity is present whenever the thermal expansion coefficient is negative, but Fetters et al.[41] have found that when the fraction of 1,2-enchainment is high, hydrogenated polybutadiene has a *positive* thermal expansion coefficient. Therefore, one would not expect hydrogenated polybutadiene with a high fraction of 1,2-enchainment to show thermorheological complexity, and our observations are consistent with the work of Levine and Milner.[16]

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